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Editorial Comment

NEW YEAR GREETINGS

THE past year has been a notable one for our Society. Beginning in unavoidable confusion and uncertainty resulting from changes of the editorial and secretarial offices, the year has seen a remarkable gain—a gain which is being reflected in the rapidly increasing membership, in the greatly enlarged scope of the Journal, and in the enthusiasm of the members, both old and new, to advance the prestige and usefulness of the Society.

One of the factors contributing to this upsurge was the twenty-fifth annual meeting of the Society, held in Rochester in October. Those who attended will always remember the inspiration and pleasure of those three days. An account of the meeting was given in last month's issue of the Journal. The Society is greatly indebted to those who contributed so loyally and faithfully to the success of that meeting. Not all can be named, but special acknowledgment is due to the two committees in charge—the committee on meetings and program, Dr. Kenney, Chairman, which arranged for the excellent group of invited papers and the instructive and entertaining lecture by Dr. Land, and the local committee appointed by the Rochester Section of the Society, Mr. Foster, Chairman, which took care of the innumerable details contributing to the convenience and pleasure of those attending. None of us will forget the dinner at the Oak Hill Country Club so generously arranged for the Society by the Bausch and Lomb Optical Company, which provided the ideal setting for recognition of our charter members and for presentation of the first Adolph Lomb Medal to Dr. MacAdam.

Not every meeting of the Society can be a twenty-fifth annual meeting. But every meeting can be a good meeting if only the members contribute and attend in good number. So now let us look to the coming February and October meetings. Next month we meet in Cambridge with the American Physical Society. In October we meet with the other founder societies in New York to celebrate the tenth anniversary of the American Institute of Physics. Keep these dates in mind and plan to be present.

During the past year the Society has had a net gain of more than 250 members. This remarkable record is a result of several things. First, we have an active and progressive membership committee under the leadership of Miss Nickerson which is steadily obtaining new members for the Society. One of her aims is to make every member conscious of his responsibilities to the Society in this respect. Doubtless each of us knows several individuals interested in one or more of the many branches of optics but not now members of our Society. The ideal method is for us to approach these prospective members ourselves, but if for any reason that does not seem feasible let us by all means send their names to the membership committee.

Another factor in our present rapid growth is the efficient conduct of the secretary's office. Professor Hardy has always been active in ob-

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taining new members, and his systematizing abilities enable him to assist the various committees and officers of the Society with great effectiveness. Nor should we overlook the continued tireless service of our treasurer, Mr. Kurtz, who never forgets to collect our dues.

A third and most important reason for the large increase in membership and for the present favorable outlook in the affairs of the Society relates directly to the editor's office. A year ago we anticipated that our then new editor would lead the *Journal of the Optical Society of America* "into new fields of usefulness and influence." We now see this taking place and we can congratulate ourselves that Professor Harrison has accepted reappointment as editor for a four-year period. The increased coverage of the Journal for 1940 and the plans for 1941 were noted in the November editorial. The inclusion of a section on Applied Spectroscopy, announced at that time, becomes a reality in the present issue. Inspection of the list of associate editors shows that six new names have been added, primarily to cover this field. As a direct result of this progressive policy, a large number of new members interested in the spectroscopic and spectrophotometric analysis of materials have joined our Society.

But we cannot be content. The cost of publishing the enlarged Journal, combined with loss of revenue from foreign subscriptions, makes it imperative that we secure more new members in 1941.

We welcome all of our new members most heartily. For most of them this is their first issue of the Journal. We hope they will find it a source of interest and profit. In return, we hope they will contribute to its continuing progress and increasing scope by publication in its pages. We hope they will find opportunities for cooperative action and wider acquaintance among those in the Society who are interested in their respective branches of optics.

A noteworthy example of such interest and cooperation within the Society is afforded by the activities of those interested in the field of colorimetry and its applications. The report on colorimetry, now nearing completion by a committee under the chairmanship of Dr. Jones, was noted in last month's editorial. The Society is also further contributing to the advancement of colorimetry by its active support of the Inter-Society Color Council, which under the leadership of Dr. Judd is securing valuable cooperation in colorimetric matters among eleven technical societies and organizations. Including our ten official delegates, about fifty members of the Optical Society are affiliated with the Inter-Society Color Council in one connection or another.

In the past there have been many such committees and groups interested in the varied fields of optics—geometrical, physical, and physiological optics, radiometry, spectrophotometry, pyrometry, photography, and others. At present many of our members, both old and new, are especially interested in the preparation of a glossary of optical terms and in fields relating to visual processes and the biological effects of radiation, in addition to the large group interested in applied spectroscopy. Many of our members are cooperating in national defense activities.

It is our earnest desire that everyone, whatever his special interest, may find a place of service in the Society and that the associations may be of benefit both to him and to the Society. We all have a great opportunity, now while the momentum is high, to advance the Optical Society of America to heights of influence and service never before attained. May it be a happy New Year!

K. S. GIBSON
President

The Distribution of Energy in the Visible Spectrum of Daylight

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(Received October 29, 1940)

ALTHOUGH sunlight is our oldest illuminant, relatively little work has previously been done to determine the distribution of energy in its visible spectrum. Some data have been obtained by the Smithsonian Institution and reported in the literature,[1–3] but they do not include results for a wide variety of conditions. Gibson[4] has described a method of computation to obtain spectral energy distributions for various proportions of sunlight and skylight. Since experimental data regarding natural daylight are necessary for a complete appraisal of artificial daylight, the authors have undertaken the measurement of spectral distribution of energy for various types of natural daylight in the vicinity of Cleveland.

All of the data given in this paper were obtained about nine miles from the center of the city. The atmospheric conditions are neither the best nor the worst to be encountered in practice. The atmosphere contains less smoke and dust than in many urban locations, but Cleveland has a great deal of cloudy weather, particularly during winter months, and the sky is seldom completely free of some haze and smoke.

It is not always possible to describe accurately the type of daylight measured. The sky may be cloudless but haze, dust and smoke in the atmosphere, even in small amounts, may appreciably reduce the color-temperature* of the light from the sky. The presence of clouds will usually reduce it also, since sunlight reflected from the clouds will have a lower color-temperature than light from the sky itself. Such changes in spectral distribution usually take place very gradually and anyone using daylight for critical color-matching or discrimination may be unaware that the light is changing unless a cloud suddenly obscures the sun.

The measurement of spectral energy distribution of daylight requires very sensitive energy-measuring apparatus with which rapid measurements can be made, since in many cases the illumination and spectral quality may change very appreciably in a short time. For their measurements the authors used a Hilger constant-deviation spectrometer with a caesium phototube and suitable vacuum-tube amplifier. The sensitivity could be quickly changed by changing to a different resistance in the grid circuit of the detector tube. In some of the tests the sensitivity of the amplifier was kept constant and a neutral filter used to reduce the incident energy when necessary. Figure 1 is a photograph of the apparatus in use on the roof of our laboratory in East Cleveland. The spectrometer was directed at a magnesium oxide disk for all measurements except those of direct sunlight and of zenith sky. A camera shutter, with bulb control, served to interrupt the light entering the collimator slit.

The complete apparatus was calibrated by use of a 1000-watt projection lamp which had been standardized for color temperature at the National Bureau of Standards. Blackbody energy distribution for the assigned color temperature was assumed. The lamp bulb was slightly selective in transmission, but no correction has been applied for this factor. Correction for this selectivity would slightly reduce all energy values for wave-lengths shorter than λ4400. A 5-mm Corning No. 590 "daylight" glass filter was used between the lamp and spectrometer during the calibration, to make the energy distribution comparable to that of the daylight energy to be measured and thus reduce possible errors due to stray light. These methods of calibration eliminated the necessity for determining and correcting for dispersion and selective transmission of

[1] C. G. Abbott, F. E. Fowle and L. B. Aldrich, "The distribution of energy in the spectra of the sun and stars," Smithsonian Miscellaneous Collections, 74, No. 7.
[2] Herbert H. Kimball, "The distribution of energy in the visible spectrum of sunlight, skylight and the total daylight," *Proceedings International Congress on Illumination*, 1928, p. 501.
[3] H. P. Gage, "Spectral distribution of solar radiant energy," Trans. Ill. Eng. Soc. **34**, 316 (1939).
[4] Kasson S. Gibson, "Approximate spectral energy distribution of skylight," J. Opt. Soc. Am. **30**, 88A (1940).
* The color temperature of any non-blackbody has been defined as the temperature at which it is necessary to operate a blackbody so that its radiation will match in integral color that of the source studied.

FIG. 1. Photograph of apparatus used to measure the spectral distribution of energy in daylight.

the spectrometer and for spectral sensitivity of the photo-tube.

Although a complete distribution, from λ4000 to λ7000, could be measured in 15 to 30 minutes, some changes in spectral energy distribution might occur during the measurements, especially if made during a period of the day when the sun was changing in altitude quite rapidly. Consequently, in many cases measurements of energy distribution were made at intervals of 100 or 200 angstroms throughout the visible spectrum, from λ4000 to λ7000, then repeated in the reverse direction and the two runs averaged. To correct for changes in illumination during the measurements three methods were used: First, the spectrometer was reset at λ5600 frequently during a run, and the assumption made that the energy at any other wave-length varied at the same rate as that at λ5600; second, a Weston light meter was used to measure changes in daylight illumination; third, another photo-tube was used with a special filter to measure a narrow band of energy centered at λ5600. This filter,[5] composed of four different types of glass, is very effective in ex-

[5] Kasson S. Gibson, "Filter for obtaining light at wave-length 560 mμ," J. Opt. Soc. Am. **25**, 131 (1935).

TABLE I. *Average color-temperatures of daylight for various seasons and weather conditions (light received on a horizontal plane).*

	APRIL AND MAY	JUNE AND JULY	SEPT. AND OCT.	NOV., DEC. AND FEB.
Direct sunlight alone, 9 A.M. to 3 P.M.	5800°K	5800°K	5450°K	*5500°K
Direct sunlight before 9 and after 3	5400	5600	4900	*5000
Sunlight plus light from clear sky				
9 A.M. to 3 P.M.	6500	6500	6100	*6200
before 9, after 3	6100	6200	5900	5700
Sunlight plus light from a hazy or slightly overcast sky	5900	5800	5900	5700
Sunlight plus skylight—25 to 75 percent overcast	6450	6700	6250	—
Totally overcast skylight	6700	6950	6750	—
Light from hazy or smoky sky	7500	8150	*8400	7700
Light from clear blue sky				
9 A.M. to 3 P.M.	26000	14000	12000	*12000
before 9, after 3	27000	—	—	12000

* One observation.

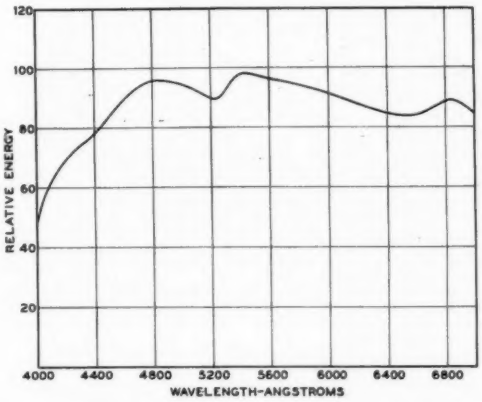

FIG. 2. Spectral distribution of energy in direct sunlight, 10/3/39, color temperature 5335°K.

cluding all energy except that in the desired band, and measurements made with it correlate very closely with those made with the spectrometer set at λ5600. It is especially useful in measurements of light from an overcast sky, when the illumination may change by a factor of three or four during a period of half an hour. Data given on the various figures, especially those shown on Fig. 8, indicate that the energy in a narrow band at λ5600 is almost directly proportional to the illumination in footcandles for a wide range of spectral distribution of daylight.

About ten years ago one of the authors, by a method using color filters, measured the color temperature of various types of daylight over a period of a year. The average results of that study are shown in Table I.[6] The results of the present research are in very good agreement with the previous study except that in no case was a color temperature as high as 6500°K found for sunlight plus light from a clear sky on a horizontal plane. This was probably due to more haze and smoke in the atmosphere during the later measurements, since no measurements were made when the sky was entirely free from haze or smoke, even though cloudless.

The spectral energy distribution of direct sunlight on a clear day in October at about 10:00 to 11:00 A.M. (all our measurements were made between 9:30 A.M. and 3:30 P.M.) is shown by the

[6] A. H. Taylor, "The color of daylight," Trans. I. E. S. 25, 154 (1930).

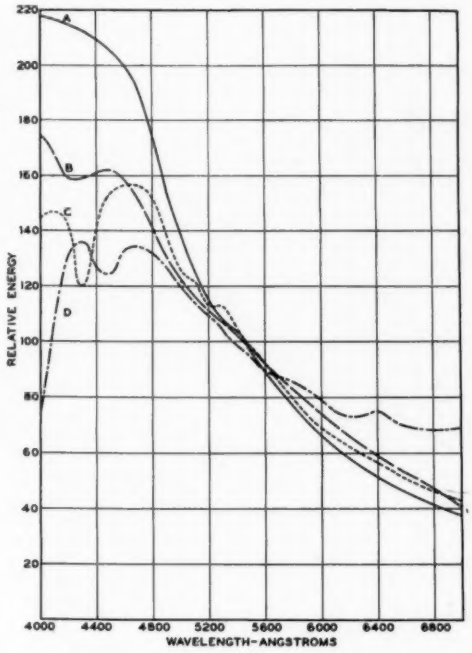

FIG. 3. Spectral distribution of energy from the zenith sky. (A) 9/18/39, sky very clear, color temperature 60,000°K. (B) 9/14/39, P.M. sky hazy and smoky, color temperature 13,000°K. (C) 8/8/40, sky clear but smoky, color temperature 12,200°K. (D) 9/14/39, A.M. sky hazy and smoky, color temperature 8,800°K. These and all other curves are plotted on the basis of *equal illumination*.

curve in Fig. 2. The computed color temperature was 5335°K. The sky is much more blue than the sun and consequently its color temperature is much higher. In Fig. 3 are presented the spectral energy distribution curves for the zenith sky on four different days. On a very clear day the sky is very blue, and on the clearest day when measurements were taken the color temperature was 60,000°K.

Light from the north sky is ordinarily less blue than that from the zenith sky, because it reaches us through more haze, smoke and dust; hence its color temperature is lower. This is clearly shown by the four curves in Fig. 4, for north skylight incident on a 45° plane. When the sky is partly or completely overcast, the light received on a horizontal plane is a mixture of sunlight and skylight filtered through the clouds, the proportions of the two being dependent upon many variable factors. The clouds are probably non-

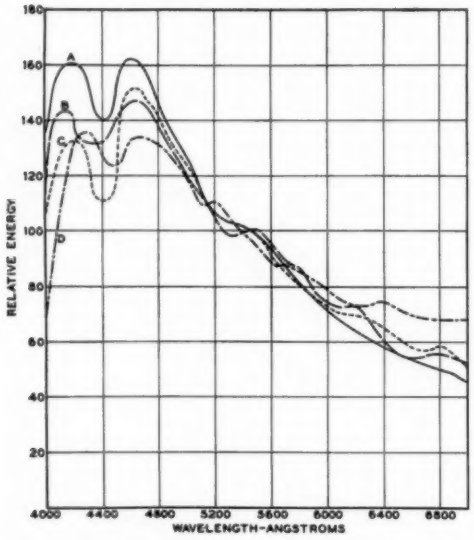

FIG. 4. Spectral distribution of energy from north sky incident on a 45° plane. (A) 9/18/39, sky clear, color temperature 12,600°K. (B) 8/8/40, sky clear but smoky, color temperature 10,000°K. (C) 9/28/39, sky clear but smoky, color temperature 9,640°K. (D) 11/15/39, sky clear but very smoky, color temperature 8,770°K.

selective in their spectral transmission in the visible spectrum, hence act to diffuse the light rather than to affect its color by selective filtering. Fig. 5 gives energy distribution curves for a partially overcast sky and for two days when the sky was completely overcast.

In Fig. 6 are given three curves showing the spectral distribution of energy on a horizontal plane from sun and sky combined on days when the sky was cloudless. Since the sun contributes over 80 percent of the light, it is obvious that the color temperature of the resultant light would be much nearer to that of sunlight than that of skylight.

Smoke and dust are selectively transmitting in favor of the longer wave-lengths. Consequently, their effect is to absorb the blue and thus reduce the color temperature of the resultant light. This is clearly demonstrated by the data for two days when the sky was cloudless but very smoky, Fig. 7.

Since for many purposes *average* data are of more interest than those for specific days, averages for the curves of Figs. 2 to 7 have been plotted as a family of curves in Fig. 8 and the detailed data given in Table II.

Fig. 9 shows the loci, on the I.C.I. colorimetry diagram, of the points for the various phases of daylight measured, also the Planckian blackbody locus. It will be noted that most of the points are slightly above the blackbody locus, i.e., the daylight is slightly yellow-green with respect to the blackbody nearest it in color temperature. Color temperatures given for the various curves are approximate for those conditions where the points do not coincide with the blackbody locus.

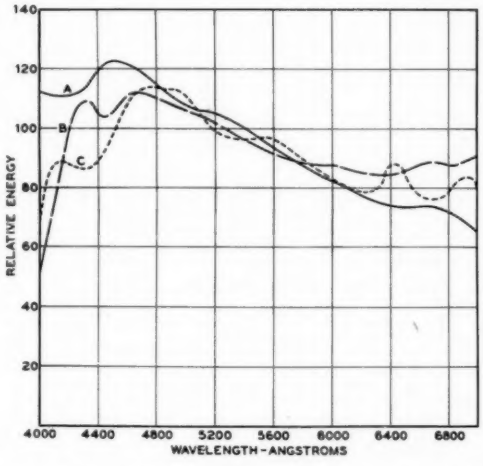

FIG. 5. Spectral distribution of energy on a horizontal plane illuminated by light from (A) a 75 percent overcast sky, 9/13/39, color temperature 7600°K; (B) a completely overcast sky, 10/11/39, color temperature 6510°K; (C) a completely overcast sky, 8/27/40, color temperature 6490°K.

As previously stated, all of the energy distribution curves shown have been plotted on an *equal illumination* (equal footcandles) basis to facilitate direct comparisons. Some of the curves show dips at approximately λ4400 and λ5100. After noting these in the earlier data, measurements were made at shorter intervals in those regions in subsequent tests. Evidence seems to indicate that these variations from smooth curves may be due to foreign matter, such as dust or smoke, in the atmosphere.

Erratic dips and humps in some of the curves at other points may be due to experimental errors, but the dips at approximately λ4400 and λ5100 occur in a considerable number of the curves and are definitely not due to experimental error.

The results given above show some of the normal variations in spectral distribution of energy in daylight, though not the whole range encountered in nature, since it is unlikely that they include data for the clearest or the least clear atmosphere. However, it is possible to cover almost the whole range shown in Fig. 8 in a day or two for a single position which receives direct sunlight for part of the day and skylight all the day. Yet one is seldom conscious of any material change in spectral quality of the daylight, even though the illumination may vary from a few footcandles to thousands. Such variations in spectral distribution materially affect the colored appearance of objects illuminated by the daylight but in general the appraisal of color is relative rather than absolute and hence is not greatly affected by the changes. In some special cases, however, it is claimed that observers doing specialized color grading carry absolute color in mind, so that they need not refer to standards frequently. In such cases it is obvious that natural daylight may be far from satisfactory for very exacting work, and a suitable artificial daylight will be much better as regards constancy of quality and quantity. Natural daylight has the advantage of greater diffusion than is usually obtained with artificial light, and this may be one reason why it is often preferred.

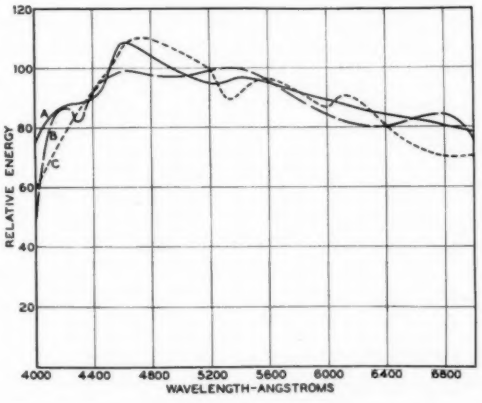

FIG. 6. Spectral distribution of energy on a horizontal plane illuminated by the sun and a fairly clear sky (A) on 9/28/39, color temperature 5960°K; (B) on 9/14/39, color temperature 6040°K; (C) on 8/21/40, color temperature 6100°K.

It is often stated that light from a north sky is more constant in quality than that of any other daylight, but Fig. 4 shows the fallacy of this statement. Our previous research[6] showed that the most constant quality of daylight would be obtained on a horizontal plane exposed to both sun and sky. Consequently if one desires to use

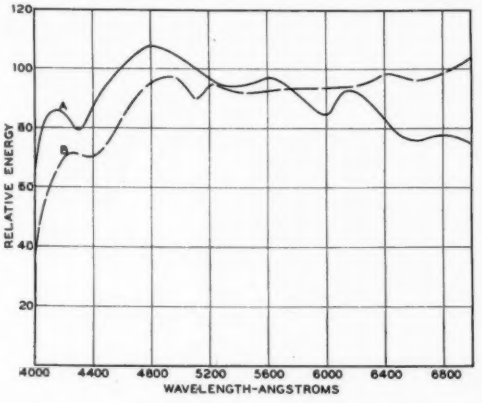

FIG. 7. Spectral distribution of energy on a horizontal plane from sun and sky when the sky was cloudless but very smoky. (A) on 8/8/40, color temperature 5680°K; (B) on 11/15/39, color temperature 4975°K.

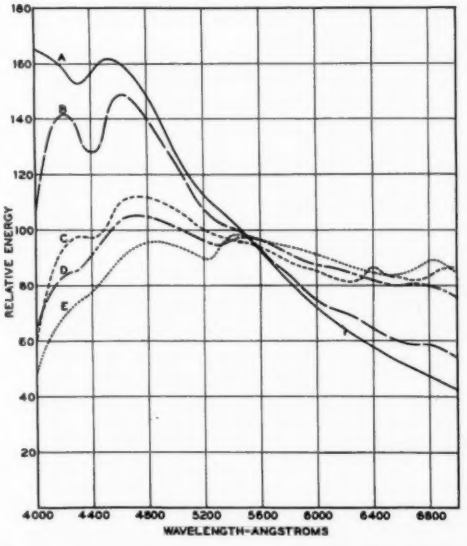

FIG. 8. *Average* energy distribution curves for the types of daylight shown on Figs. 2, 3, 4, 5 and 6. (A) Zenith sky, color temperature 13,700°K. (B) North sky on 45° plane, color temperature 10,000°K. (C) Totally overcast sky, color temperature 6500°K. (D) Sun plus sky on horizontal plane, color temperature 6000°K. (E) Direct sunlight, color temperature 5335°K.

TABLE II. *Relative spectral energy distribution of five phases of natural daylight (averages), for which the curves are shown in Fig. 8, on the basis of equal illumination.*

λ	DIRECT SUNLIGHT	SUN PLUS SKY, HORIZONTAL PLANE	OVERCAST SKY	NORTH SKYLIGHT ON 45° PLANE	ZENITH SKY
			Relative energy		
4000	49	63	59	105	165
4100	62	76	81	133	162
4200	69	84	94	142	159
4300	74	86	98	136	153
4400	78	91	97	128	158
4500	83	98	101	138	162
4600	90	104	110	149	161
4700	94	105	112	146	156
4800	96	105	112	139	148
4900	96	103	110	132	138
5000	96	101	108	123	127
5100	93	99	104	117	120
5200	90	96	100	107	112
5300	94	95	98	103	108
5400	98	96	97	101	103
5500	98	97	96	98	98
5600	96	97	94	93	92
5700	96	94	92	88	86
5800	94	92	89	84	81
5900	93	89	87	79	76
6000	92	87	85	75	71
6100	90	87	83	72	67
6200	89	85	82	70	64
6300	87	84	82	68	60
6400	85	82	86	65	57
6500	84	80	84	62	54
6600	83	80	83	59	52
6700	84	80	82	59	50
6800	88	80	83	58	47
6900	87	78	86	57	45
7000	85	76	86	54	42
			Trilinear coordinates, I.C.I. Colorimetry system		
x	0.336	0.322	0.313	0.278	0.263
y	.350	.335	.328	.294	.279
z	.342	.343	.359	.429	.458
			Color temperature		
	5335°K	6000	6500	10000	13700

daylight for color matching or discrimination, the most constant quality would be obtained by use

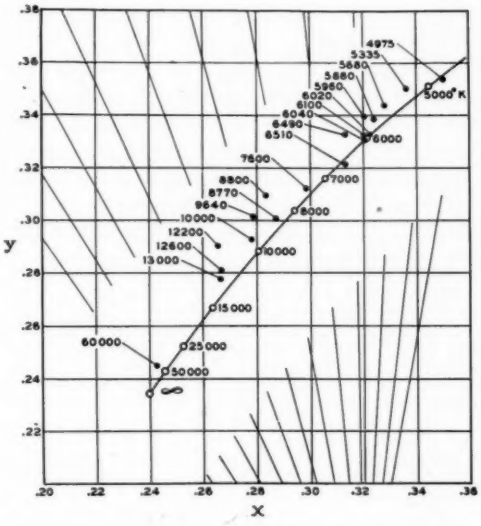

FIG. 9. Section of the I.C.I. Colorimetry diagram, showing the location of points representing various phases of daylight with respect to the blackbody line. The diagonal lines represent various values of "micro-reciprocal degrees" (mireds).

of a diffusing skylight, approximately horizontal, exposed to both sun and complete sky. The color temperature of this daylight normally varies over the range from approximately 6000 to 7000°K, with an average value of about 6500°K. The spectral distribution of energy from the fluorescent Mazda daylight lamp has been standardized to produce this color temperature. Careful tests have shown that for most applications the fluorescent daylight lamp is an excellent substitute for "average" natural daylight. Color temperatures between 6500 and 10,000°K are readily obtainable by suitable combinations of fluorescent daylight and blue lamps. Such combinations give colors which fall very close to the blackbody curve of Fig. 9.

Reflection Characteristics with Polarized Light

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(Received October 18, 1940)

1. INTRODUCTION

UNTIL the recent development of synthetic polarizing materials, applications of polarized light were confined to the laboratory and were limited by the small size and high cost of polarizing equipment. Today, however, the use of polarized light becomes more and more common, and the many new applications create new problems for research. Polarized light seems particularly promising in improving the readability of printed matter and in eliminating glare from automobile headlights.

Reflected glare from paper is very troublesome and results in much eyestrain. The trouble can be completely eliminated by proper placement of the light sources; but this solution of the difficulty is not always feasible, in which case polarized light can be used. A simple qualitative test proves that when the light source is incorrectly placed, readability can be improved by the use of a luminaire emitting polarized light; but no quantitative information on the subject has hitherto been available.

In the second of the applications listed above—the application to motor vehicles—the practicability of the scheme depends greatly on the degree to which light stays polarized through the process of reflection. Again, knowledge of the reflection characteristics of surfaces is needed.

This paper presents experimental results on the reflection characteristics of paper and printing ink illuminated with natural and with polarized light. It also gives some data on the reflection of polarized light from three samples of cloth used for men's suits.

2. PROCEDURE

All data were obtained by means of the photoelectric goniophotometer of the Illuminating Engineering Laboratories at Massachusetts Institute of Technology.* A description of the apparatus has been given in a previous paper.[1] Polaroid disks are used to polarize the incident beam and to analyze the reflected beam. Radiant energy outside the wave-length limits of 0.49μ and 0.65μ is eliminated by means of filters,[2] since Polaroid does not polarize satisfactorily beyond these limits.[3] The light-sensitive detector is a No. 782 Electrocell used with a compensating circuit.

The reflection factors considered in this paper are *diffuse reflection factors*[1] defined by the equation:

$$\rho_d(\theta_1, \theta_2) = \pi B_r(\theta_1, \theta_2)/E(\theta_1),$$

where θ_1 is the angle of incidence and θ_2 is the angle of view, both measured from the normal to the test surface. Actual values were obtained by a comparison method, the goniophotometer being calibrated by use of a Macbeth test plate, of known reflection factor, measured at normal incidence. Values of $\rho_d(\theta_1, \theta_2)$ above 100 percent are often obtained and do not imply a refutation of the conservation of energy principle. Values as high as 4.00 are shown in Fig. 3.

3. REFLECTION CHARACTERISTICS OF PAPER

Tests were made on various kinds of paper to compare the reflection characteristics of printed matter under natural and polarized light. As might be expected, the most interesting results were obtained on glossy paper, and only these tests will be described in the present treatment.

It is a well-known fact that perfectly specular reflection from the polished surface of a dielectric results in complete plane polarization at the polarizing or Brewster angle, and partial polarization at most other angles. Also, if the incident light is plane-polarized, the reflection factor of the surface is smaller or larger than the reflection

* The author wishes to express his gratitude to Professor Parry Moon, through whose cooperation this investigation has been possible.

[1] P. Moon and J. Laurence, "Construction and test of a goniophotometer," J. Opt. Soc. Am., to be published.
[2] W. W. Coblentz, "Radiometric investigations on light filters," Bur. Stand. Bull. **7**, 619 (1911).
[3] M. Grabau, Optical properties of Polaroids," J. Opt. Soc. Am. **27**, 420 (1937).

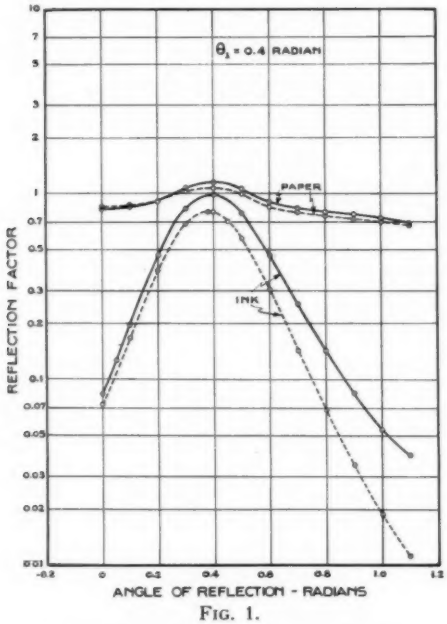

FIG. 1.

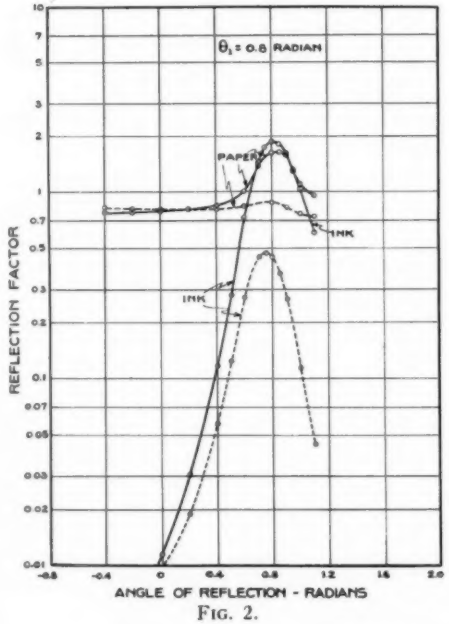

FIG. 2.

factor with natural light, depending on whether the electric vector of the incident light is parallel to the plane of incidence or normal to it.[4]

[4] Parry Moon, "A table of Fresnel reflection," J. Math. Phys. **19**, 1 (1940).

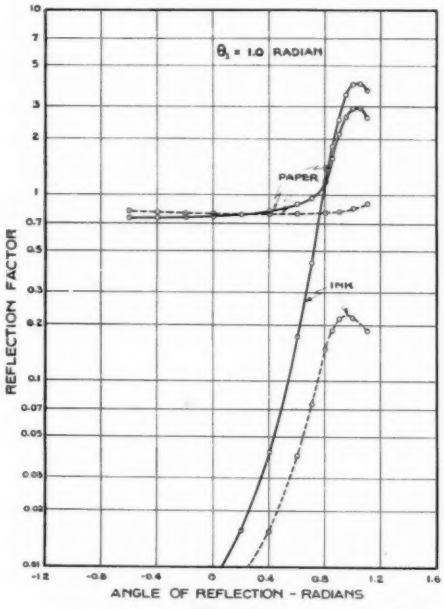

FIG. 3.

FIGS. 1, 2, 3. Reflection characteristics of white paper (as used in the *Journal of the Optical Society of America*) and black ink on the same paper. Full lines are for natural light and broken lines are for polarized light with **E** vector in the plane of incidence.

On the other hand, if the surface is not perfectly specular, there is difficulty in reaching, from theoretical considerations, any definite conclusions about reflection characteristics. The surface of paper is not perfectly smooth, and a large part of the incident light penetrates into the body of the material where it is scattered and depolarized to a considerable extent. Thus the effect of polarizing the incident light can be found only by experiment.

Since the readability of printed matter depends on the contrast between the characters and their background, it is interesting to compare the reflection characteristics of black printing ink with those of the paper on which the ink is applied. Figures 1, 2 and 3 show some of the results obtained with the glossy paper used by the *Journal of the Optical Society of America*. The test on ink was made by applying black printing ink to the same paper by means of a printer's roller. The curves in broken lines show the results obtained when the incident light is polarized with its **E** vector parallel to the plane of incidence,

whereas the continuous curves are for natural light. Figure 1 shows that when the angle of incidence is 0.40 radian and the angle of view is near zero, the diffuse reflection factor $\rho_d(\theta_1, \theta_2)$ is almost the same with either kind of light. Near the angle of specular reflection ($\theta_2=0.4$), $\rho_d(\theta_1, \theta_2)$ reaches a maximum of over 100 percent, the reflection factor being slightly higher with natural light than with polarized light. The ink shows similar characteristics but to an exaggerated extent. With natural light, the reflection factor of the ink increases from approximately 0.08 at $\theta_2=0$ to almost 1.00 at $\theta_2=0.4$. The contrast between paper and ink at $\theta_2=0.4$ is low, seeing conditions are very poor, and polarizing the light does not greatly improve matters.

Figure 2 shows the result of increasing the angle of incidence to $\theta_1=0.8$ radian. With natural light, the ink now becomes brighter than the paper at $\theta_2=0.8$. At this angle of view, conditions with polarized light are considerably better than with natural light. A more extreme case is shown in Fig. 3. The minimum contrasts for natural and for polarized light are given in Table I.

The results prove that polarized light gives improved visibility of black printed characters on glossy white paper, under the rather peculiar condition of large angle of incidence and large viewing angle (in the neighborhood of one radian). The curves show, however, that much better results would be obtained by using natural light, with correct placement of the luminaire. Of course if one insists on the common but asinine practice of placing the desk lamp directly in front of him on his desk, then he should by all means use polarized light.

4. Depolarization by Reflection

Most of the tests on the degree of depolarization of light by reflection were made on samples of gray worsteds. The incident light was found to be approximately 99.5 percent plane-polarized. Measurements were made with the **E** vector of the incident beam in the plane of incidence and also normal to it. Readings were taken with the analyzing Polaroid normal and then parallel to the plane of incidence, and the degree of polarization of the reflected beam was taken as the ratio of the difference of these readings to their sum. No correction was made for the fact that the Polaroids did not provide complete polarization.

Figures 4, 5, 6 and 7 show the results obtained on the following three samples of gray worsteds,[1] made by Cornwall Mills, Incorporated, Holyoke, Massachusetts:

Sample 100	"Sky gray"	(light)
Sample 102	"Dover gray"	(medium)
Sample 104	"Oxford gray"	(dark).

The symbols accompanying the curves refer to the plane in which the **E** vector of the incident beam vibrates with respect to the plane of incidence.

The light reflected from the darkest sample is almost completely plane-polarized, and the degree of polarization decreases as the reflection factor is increased. Undoubtedly the amount of depolarization is intimately associated with the amount of light that is reflected from the body of the material. The oxford gray cloth is dyed almost black; so practically all the light that penetrates the surface of the wool fibers is absorbed. The reflected light comes from surface reflection and is of a pseudospecular nature, resulting in very little depolarization. With the sky gray cloth, however, most of the reflected light comes from the interior of the material, where it has had considerable opportunity to become depolarized by numerous reflections.

Measurements of the same nature were made on samples of white and black chalkboards, and the same general conclusions were found to apply. Finally a metallic surface was tested, the sample being a piece of Alzak aluminum with diffusing finish. The results indicate that light is but slightly depolarized by reflection and that the plane of polarization of the incident light has very little influence on the degree of polarization of the reflected light.

Table I.

Angle of Incidence (radians)	Minimum Contrast: Natural Light	Minimum Contrast: Polarized Light
0.4	0.13	0.26
0.8	0	0.46
1.0	0	0.73

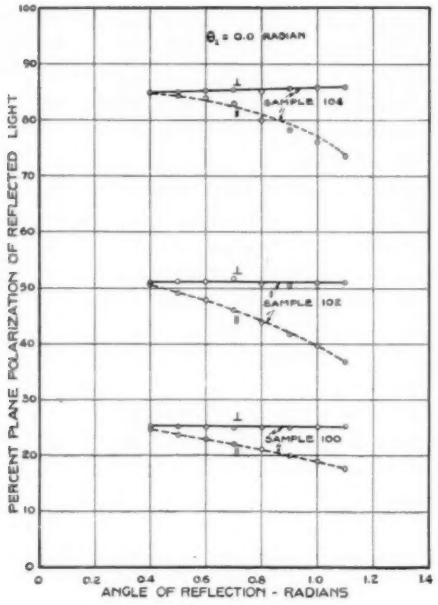

FIG. 4.

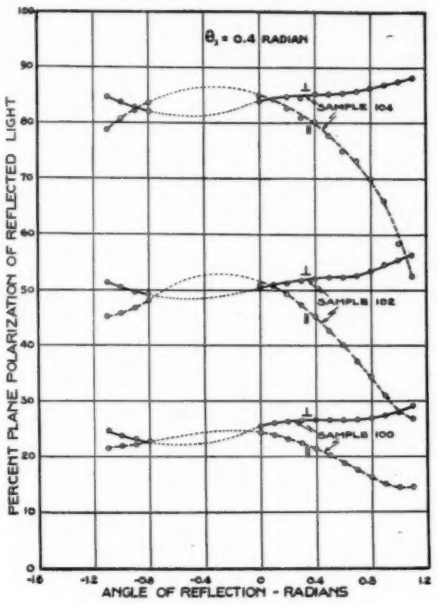

FIG. 5.

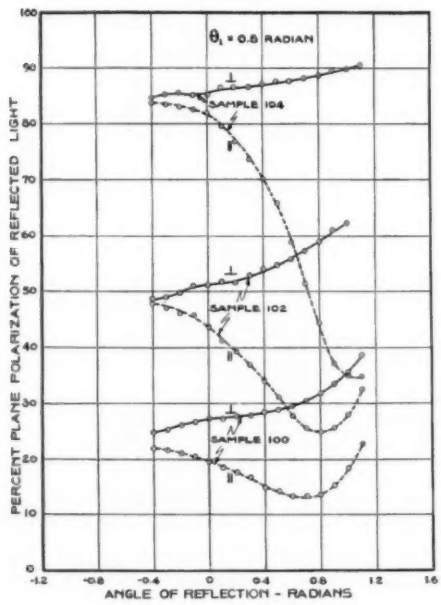

FIG. 6.

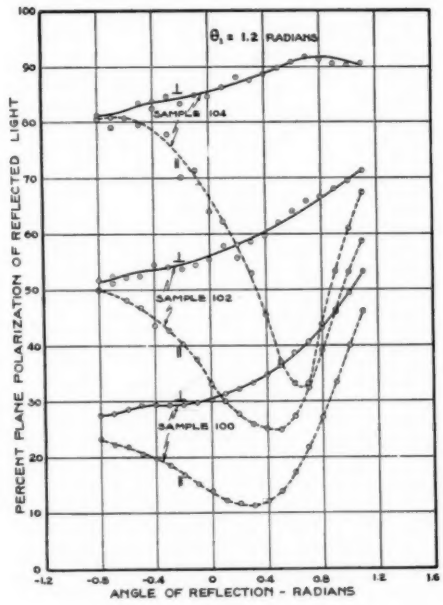

FIG. 7.

FIGS. 4, 5, 6, 7. Percent polarization of light reflected from gray cloth. Incident light is polarized. Symbols represent the plane of the **E** vector with respect to the plane of incidence.

The foregoing results show that a very fortunate state of affairs exists, as far as the use of polarized light for automobiles is concerned. Headlights and polarizing windshields have their planes of polarization parallel to each other. If reflected light from objects remains plane-polarized, it will pass through the windshield with little loss; but if depolarization takes place in the reflecting surfaces, over 50 percent of the reflected light will be absorbed by the windshield. Dark surfaces, since they cause comparatively little depolarization, will be seen much better than might be expected. On the other hand, light surfaces do not usually present a problem of visibility, so the depolarization they cause is not troublesome. The necessary candlepower for cars making use of polarized light may be computed in terms of the dark surfaces alone, the most important of these dark surfaces being the clothing of pedestrians.

5. Conclusions

Quantitative data on the reflection characteristics of printed matter under natural and polarized light are presented and discussed. The use of light whose **E** vector is polarized in the plane of incidence is found to decrease the reflected glare and to increase the contrast between the printed characters and their background.

Results on the degree of depolarization of light reflected from worsteds show that dark cloth causes little depolarization, whereas light cloth depolarizes almost completely. This conclusion may have an important bearing on the use of polarized light for motor vehicles.

Metallic surfaces depolarize very little. Moreover, the reflection factor of metals is almost independent of the plane of polarization of the incident beam, whereas the reflection factor of nonmetallic surfaces is greatly affected by the plane of polarization.

Interference Phenomena with a Moving Medium

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(Received October 14, 1940)

INTRODUCTION

STUDIES of the phenomena characteristic of optical interference have been made by several investigators by observation of the interference patterns of capillary waves on liquids. Photographs of these waves on liquids have been made and figure in optical texts.[1] These studies have demonstrated typical phenomena connected with multiple sources, reflection, refraction, and diffraction. For the most part these have been confined to the case of a source stationary with respect to the liquid. The purpose of the study here described is to consider certain of the similar problems for the case of relative motion of the source and liquid. From this study it is possible to derive, on the assumption of the invariance of the phenomena with motion, the Fitzgerald contraction, the Larmor-Lorentz change of clock rate, and the Fresnel convection coefficient.

APPARATUS AND METHOD OF OBSERVATION

Previous experimenters have used a plunger attached to a tuning fork, or similar method involving contact with the liquid (e.g., mercury) to produce the capillary waves. In order to avoid actual contact, which with a moving liquid would tend to produce a "bow wave," a mechanical contact was replaced in this work with an air jet or jets of glass tubing drawn down to a small diameter. The air stream was made intermittent by the use of disks with a chosen number of openings, rotated by a synchronous motor in a slot in the tube feeding high pressure air to the jets.

For illumination of the liquid surface, which was of mercury, either a tungsten lamp behind a small aperture with a diffusing glass was used (for continuous illumination for observing interference bands) or a neon lamp on synchronized alternating current (for observing the individual ripples). The light was made to fall normally on the mercury surface, and was observed normally by means of a semi-transparent mirror at 45°, while some distance above the surface was an achromatic convex lens which was located at its focal distance both from the lamp aperture and the camera lens aperture.

In order to secure relative motion of the air jets and the mercury surface the entire optical system with the jets was mounted on a lathe bed, with a motor drive on the screw capable of imparting velocities as high as a considerable fraction of the velocity of the capillary waves.[2] The mercury was placed in a trough mounted on an antivibration suspension, and, to prevent wall reflections, the meniscus around the mercury was filled with glycerin.

Figure 1 gives a diagram of the apparatus, which is shown also by the two photographs, Figs. 2 and 3.

PHENOMENA WITH A SINGLE JET

In Fig. 4 is shown the capillary wave system as set up by a single jet, interrupted at a frequency of 30 per second. In Fig. 5 is shown the same system when the relative velocity of medium and jet is 11.3 cm per second ($v/c=0.51$). Both are photographed by the light of a neon lamp giving 30 flashes per second. When photographed by a time exposure with the tungsten lamp the surface appears perfectly smooth, since no conditions are present to produce interference bands.

The conspicuous feature of Fig 5 is the exhibition of the Doppler effect. The wave-lengths in front of and behind the jet are

$$\frac{\lambda s}{1+(v/c)} \quad \text{and} \quad \frac{\lambda s}{1-(v/c)},$$

respectively, where λs is the wave-length for the

[1] R. W. Wood, *Physical Optics*, second edition (Macmillan, 1924), p. 129.

[2] The velocity of the capillary waves (c) varies with their frequency. For the single hole disk (30 pulses per second) the wave velocity with a relative motion of jets and mercury (v) of 11.3 cm per sec. was measured from the photographs as 22 cm/sec.

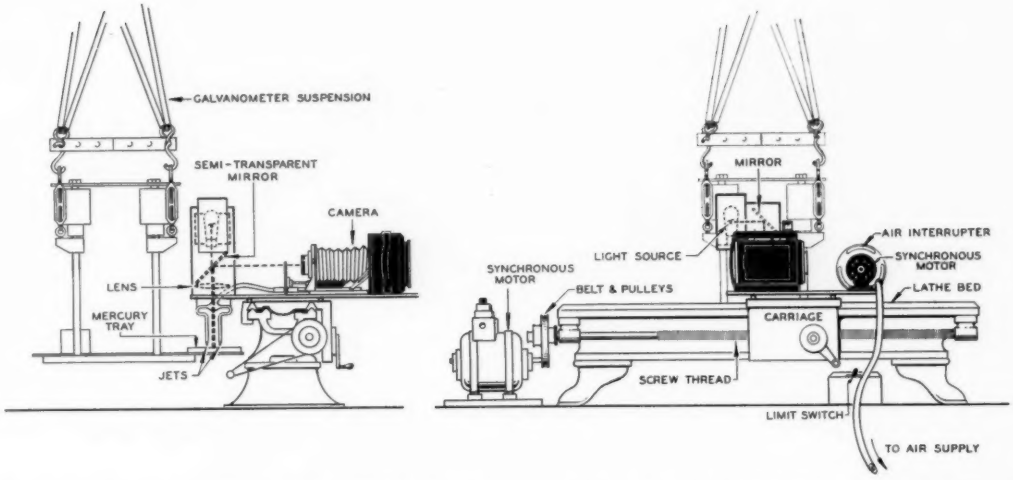

FIG. 1. Diagram of apparatus for photographing wave phenomena on mercury surface with relative motion of source of waves and liquid.

stationary condition, v the velocity of translation of the optical system, and c the velocity of the capillary waves.

INTERFERENCE BANDS BETWEEN TWO SYNCHRONIZED SOURCES

Using two jets, fed from the same interrupted air supply, we simulate the Fresnel biprism, or the Fresnel or Lloyd mirrors. The capillary wave system from such a double jet consists of intersecting wave systems of the sort formed by the single jet, which are in and out of phase with each other at definite positions with respect to the jets (Fig. 18).

In Figs. 6 and 7 are shown time exposures, in which the individual ripples are not visible. Instead we observe interference bands, showing as bright lines on a dark ground, these lines corresponding to loci of similar phase.

Several features of interest are revealed by study of these pictures. First of all we find that the interference bands are *symmetrical* in front of and behind the jets for both the stationary and moving conditions. (Heavy exposures for the moving condition are necessary to permit verification of this point, caused by a difference of intensity fore and aft, which will be discussed

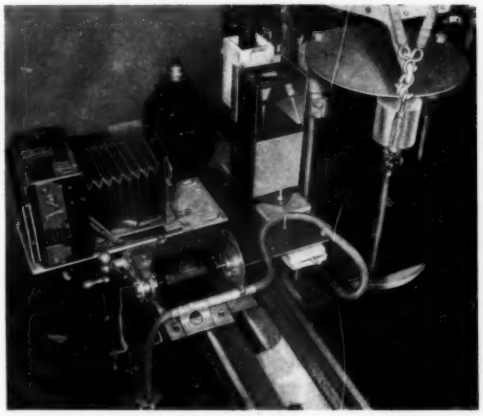

FIG. 2. Photograph of apparatus.

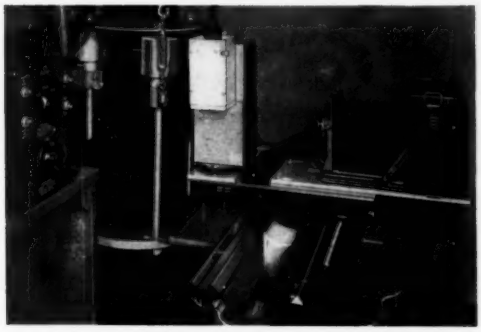

FIG. 3. Photograph of apparatus.

FIG. 4. Capillary wave system set up by single jet, stationary condition. Stroboscopic illumination. Air pulses, 30 per second.

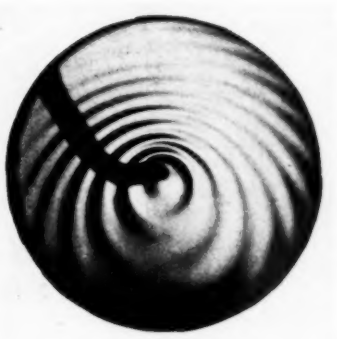

FIG. 5. Capillary wave system set up by a single jet; relative velocity of jet and mercury surface 11.3 cm per sec. ($v/c=0.51$). Stroboscopic illumination. Air pulses, 30 per second.

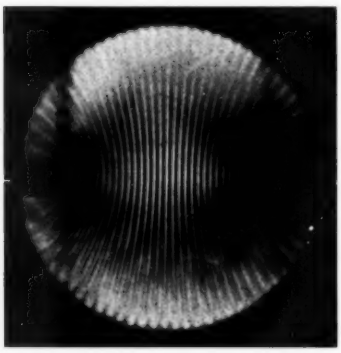

FIG. 6. Interference bands between two sources; stationary condition; continuous illumination. Air pulses, 60 per second.

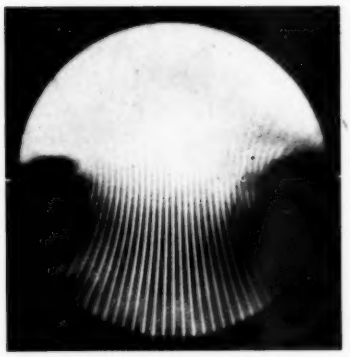

FIG. 7. Interference bands between two sources; relative speed of sources and liquid, 14.4 cm per second; continuous illumination. Air pulses, 60 per second.

later.) Secondly, we find that with the moving condition the interference bands are more numerous between the jets. This is exhibited clearly by matching the halves of prints for each condition across the line joining the jets, as shown in Fig. 8. A further difference, which is not readily seen in the photographs, but will be brought out in the discussion of the theory, is that the curvatures of the hyperbolae are somewhat different in the moving and in the stationary cases.

Other features, which will be discussed later, are the differences in intensity or visibility fore and aft, already mentioned, and the appearance, under certain conditions of air pressure and of jet form and position, of rings concentric with the jets in the stationary condition, which became ellipses in the moving condition.

THEORY OF INTERFERENCE BANDS BETWEEN TWO SYNCHRONIZED SOURCES

The theoretical presentation of these phenomena may be illuminatingly introduced by a graphical delineation of the development of the wave systems. This is done in Fig. 9 for the stationary case, where successive ripple crests are shown concentric with the source below, and as reflected from a mirror above. The loci of similar phase are shown by the dashed lines, which are

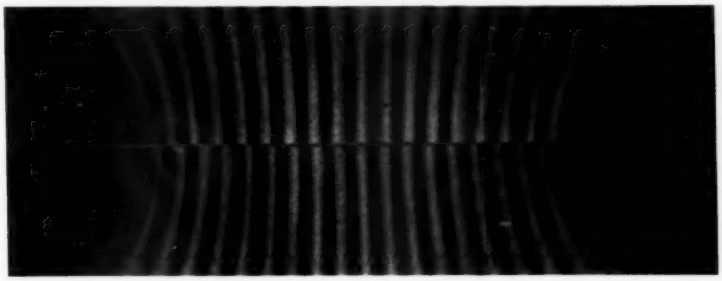

FIG. 8. Comparison of interference band spacing for stationary (upper) and moving (lower) condition.

confocal hyperbolae. The corresponding case for a moving medium is shown in Fig. 10 where the medium is moving to the left at a velocity 0.4 the wave velocity. It will be seen that the interference bands *are still symmetrical*, but, in agreement with the experimental findings, closer together, there being for the condition shown ten bands on the normal between source and mirror, as against nine for the stationary case.

By reducing the frequency of the light source it is possible to obtain again the same number of bands as in the stationary case. This is done in Fig. 11, the bands being still symmetrical. In Fig. 12 attention is concentrated on a single interference band. At A is shown the band for the stationary condition; at B for the moving condition; at C for the moving condition with a frequency chosen to restore the band to its stationary position on the normal between mirror and source. It will be seen that this band is of greater curvature than the original band A.

These relations may be developed analytically by reference to Figs. 13 and 14. In Fig. 13 the optical conditions are shown for the development of constructive interference at a point p located in the space between and below the synchronized light sources S_1 and S_2 of period τ. By inspection of the figure we write down the relation

$$\left[\left(\frac{d}{2}+x\right)^2+y^2\right]^{\frac{1}{2}}-\left[\left(\frac{d}{2}-x\right)^2+y^2\right]^{\frac{1}{2}}$$

$$=c(t_1-t_2)=n\tau c,$$

where n is the number of whole periods, τ, between the interfering waves and c the wave velocity.

In Fig. 14 the medium is moving downward with the velocity v. We have for t_1' the relation

$$t_1'=\left[\frac{\left(\frac{d}{2}+x\right)^2+(y-vt_1')^2}{c}\right]^{\frac{1}{2}}$$

and the similar relation for t_2'.

Solving for t_1' we get

$$t_1'=\frac{-\frac{yv}{c^2(1-(v^2/c^2))^{\frac{1}{2}}}+\frac{1}{c}\left[\left(\frac{d}{2}+x\right)^2+\frac{y^2}{1-(v^2/c^2)}\right]^{\frac{1}{2}}}{(1-(v^2/c^2))^{\frac{1}{2}}}$$

and similarly for t_2'

$$t_2'=\frac{-\frac{yv}{c^2(1-(v^2/c^2))^{\frac{1}{2}}}+\frac{1}{c}\left[\left(\frac{d}{2}-x\right)^2+\frac{y^2}{1-(v^2/c^2)}\right]^{\frac{1}{2}}}{(1-(v^2/c^2))^{\frac{1}{2}}},$$

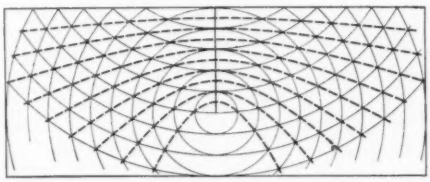

FIG. 9. Graphical representation of interference system between wave source and mirror, with stationary medium.

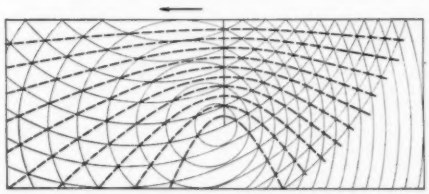

FIG. 10. Graphical representation of interference system between wave source and mirror, with moving medium.

hence

$$c(t_1'-t_2')=\frac{\left[\left(\frac{d}{2}+x\right)^2+\frac{y^2}{1-(v^2/c^2)}\right]^{\frac{1}{2}}-\left[\left(\frac{d}{2}-x\right)^2+\frac{y^2}{1-(v^2/c^2)}\right]^{\frac{1}{2}}}{(1-(v^2/c^2))^{\frac{1}{2}}},$$

which shows, by the occurrence of y only in the squared form, that the interference bands are still symmetrical. If now we put

$$y'=\frac{y}{(1-(v^2/c^2))^{\frac{1}{2}}},$$

$$\tau'=\frac{\tau}{(1-(v^2/c^2))^{\frac{1}{2}}},$$

we get

$$c(t_1'-t_2')=n\tau' c$$

$$=\left[\left(\frac{d}{2}+x\right)^2+y'^2\right]^{\frac{1}{2}}-\left[\left(\frac{d}{2}-x\right)^2+y'^2\right]^{\frac{1}{2}},$$

which is exactly of the form of the expression for the stationary condition, and is identical with it if (1) we measure distances in the y direction by a scale shortened in the ratio

$$\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}:1,$$

and if we increase the period of our sources in the ratio

$$\frac{1}{\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}}:1,$$

or reduce their frequency in the ratio

$$\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}:1.$$

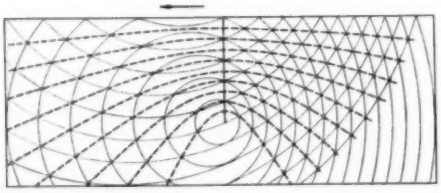

FIG. 11. Graphical representation of interference system between wave source and mirror, with moving medium; frequency of source reduced to restore stationary separation of bands along normal between source and mirror.

In terms of Fig. 12, the curve C becomes identical with A if the ordinates are measured with a scale short in the ratio

$$\left(1-\frac{v}{c}\right)^{\frac{1}{2}}:1.$$

We thus find that, if the moving interference pattern is to be identical with the stationary, we derive from these interference experiments both the Fitzgerald contraction and the Larmor-Lorentz change of clock rate with motion.

STANDING WAVES PRODUCED BY WAVES OF DIFFERENT VELOCITIES

Under certain conditions, of which the most important is high pressure in the air jet, concen-

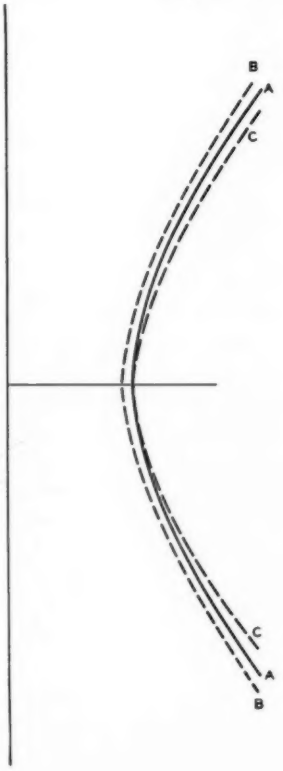

FIG. 12. Position and shape of single interference band of system between source and mirror. A, stationary medium; B, moving medium; C, moving medium, with frequency of source reduced to restore stationary condition along normal between source and mirror.

tric stationary interference rings appear about a single jet, not requiring intermittent illumination for their revelation. These rings become ellipses when the medium is in motion. These rings and ellipses are shown in Figs. 15(a) and 15(b), the photographs being time exposures with the tungsten lamp. When two jets are used the appearance of the interference pattern with the moving condition is shown in Fig. 16. Superposed on the symmetrical interference pattern previ-

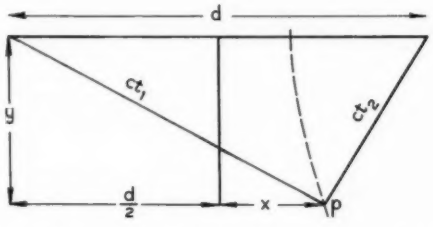

FIG. 13. Production of constructive interference between two sources; medium stationary.

ously described, from which it is impossible to detect the direction of motion, is an unsymmetrical pattern from which the direction of relative motion of jets and liquid can be learned.

The origin of these additional standing waves is made clear by observing the surface with an intermittent light set at such a speed of interruption that the ripples appear to move slowly outward from the jet. It is then observed that there are two sets of waves, traveling with different velocities, one set flowing over the other.

These two sets of waves are, respectively, the capillary waves, and the gravity waves, which, as is well known, travel with different velocities.

THEORY OF STANDING WAVE PATTERNS PRODUCED BY WAVES OF DIFFERENT VELOCITIES

The characteristics of standing waves formed by two wave systems of the same frequency but different velocities are obtained from the well-known expression for the group velocity of waves of different frequency and different velocity,[3]

[3] P. Drude, *Lehrbuch der Optik* (Hirzel, Leipzig, 1900), p. 114.

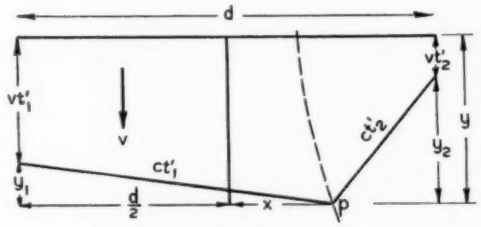

FIG. 14. Production of constructive interference between two sources; medium moving.

namely,

$$S=2A\sin\frac{2\pi}{\tau'}\left(t-\frac{x}{V'}\right)\times\cos\pi\left[t\left(\frac{1}{\tau_1}-\frac{1}{\tau_2}\right)-x\left(\frac{1}{\tau_1 c_1}-\frac{1}{\tau_2 c_2}\right)\right],$$

where c_1 and c_2 are the two velocities, and

$$\frac{1}{\tau'}=\frac{1}{2}\left(\frac{1}{\tau_1}+\frac{1}{\tau_2}\right),\quad \frac{1}{V'}=\frac{1}{2}\tau\left(\frac{1}{\tau_1 c_1}+\frac{1}{\tau_2 c_2}\right).$$

Upon putting $\tau_1=\tau_2=\tau$, we get

$$S=2A\sin\frac{2\pi}{\tau'}\left(t-\frac{x}{V}\right)\cos\frac{\pi x}{\tau_1}\left[\frac{1}{c_2}-\frac{1}{c_1}\right].$$

The envelope of the vibration of frequency τ' is a cosine curve recurring in configuration at *distances*

$$x=2n\tau\left[\frac{c_1c_2}{c_1-c_2}\right],\quad n=0,\ 1,\ 2,\ \text{etc.}$$

(the *group velocity* is zero).

If the medium is moving with velocity v, these distances became

$$x'=2n\tau\left[\frac{(c_1+v)(c_2+v)}{(c_1+v)-(c_2+v)}\right]=2n\tau\left[\frac{c_1c_2+v(c_1+c_2)+v^2}{c_1-c_2}\right].$$

These distances, containing a term in v, correspond to the distances of the interference bands from the source, in the direction of motion of the liquid, and account for the conditions shown in Figs. 15(a) and 15(b).

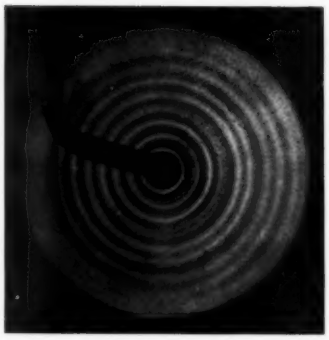

FIG. 15(a). Stationary waves produced by high air pressure, stationary medium, continuous illumination. Pulse frequency, 90 per second.

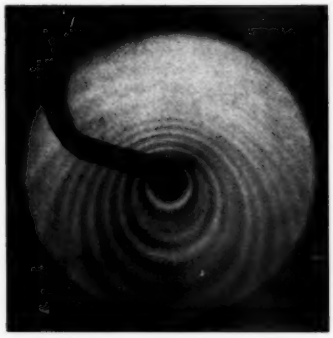

FIG. 15(b). Stationary waves produced by high air pressure, moving medium, continuous illumination. Pulse frequency, 90 per second; relative velocity of medium and source, 11.3 cm per second.

The optical case corresponding to this is produced by letting one wave system traverse a refractive medium, and observing the standing waves at the surface between the medium and free space. For the case of no motion with respect to the medium, we have, if the refractive index of the medium is μ,

$$c' = \frac{c}{\mu}$$

and

$$x = 2n\tau\left[\frac{c}{\mu - 1}\right], \quad n = 0, 1, 2, \text{ etc.}$$

For the moving case, putting c' for the velocity of the waves *with respect to the medium*

$$x = 2n\tau\left[\frac{(c+v)(c'+v)}{c-c'}\right].$$

Noting, however, that in motion τ becomes

$$\frac{\tau}{(1-v^2/c^2)^{\frac{1}{2}}},$$

and that our measured distance is greater in the ratio

$$\frac{1}{(1-v^2/c^2)^{\frac{1}{2}}} : 1,$$

this becomes

$$x' = \frac{2n\tau}{1-v^2/c^2}\left[\frac{(c+v)(c'+v)}{c-c'}\right].$$

If now we assume that this is to reproduce the stationary condition, we must have

$$2n\tau\left[\frac{c}{\mu-1}\right] = \frac{2n\tau}{(1-v^2/c^2)}\left[\frac{(c+v)(c'+v)}{c-c'}\right]$$

from which

$$c' = \frac{c/\mu - v}{1 - v/c\mu},$$

which, when v/c is small, becomes

$$c' = \frac{c}{\mu} - v\left(1 - \frac{1}{\mu 2}\right)$$

in which the coefficient of v in the second term

FIG. 16. High air pressure interference pattern between two jets with moving medium.

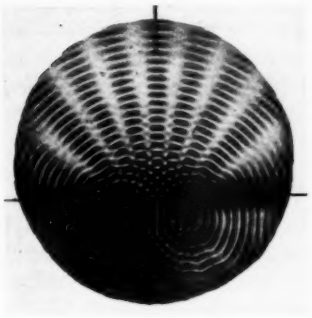

FIG. 17(a). Ripple pattern between two jets; stationary medium.

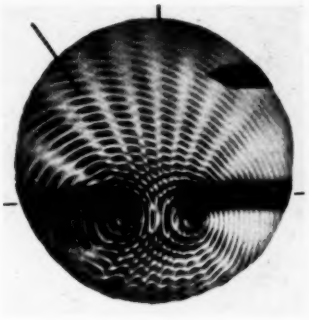

FIG. 17(b). Ripple pattern between two jets, medium moving parallel to line between jets.

will be recognized as the Fresnel convection coefficient.

We therefore find, from this study of interference phenomena with a moving medium, that if we seek the conditions which will nullify the observed effects of motion, we are led to the Fitzgerald contraction, the Larmor-Lorentz change of clock rate, and the Fresnel convection coefficient.

MEDIUM MOVING PARALLEL TO LINE BETWEEN JETS

Thus far all the interference phenomena studied with a pair of sources have been concerned with the case of motion of the medium perpendicular to the line joining the jets, corresponding to the Fresnel biprism. When the medium is moving parallel to this line, we have a condition corresponding to the case of a plane wave front, parallel to the line, falling upon two small apertures. The ripples and fringes produced by two jets with this motion of the mercury present some features of interest.

FIG. 18. Capillary wave system from two sources; relative speed of sources and medium 16 cm per second ($v/c=0.725$). Pulse frequency, 30 per second. Symmetrical dark ground illumination.

The ripple pattern, which also exhibits clearly the interference fringes, is shown in Fig. 17(a) for the stationary medium, and in Fig. 17(b) for the medium moving at approximately 0.7 the ripple velocity, in the direction indicated by the pointer. It will be noted that in each case we have a series of hyperbolic interference bands radiating from the space between the jets. When examined closely it is evident that the fringe system for the moving condition is not symmetrical. The position of the central ripple band (indicated by the black line in Fig. 17(b)), for the stationary medium, is occupied by a node for the moving medium at this velocity.

More complete information is obtained by deriving, in the same way that we obtained the equations for the previous case, the equation of the central ("white") fringe. This gives for x, the distance of the fringe from the perpendicular bisecting the line joining the jets

$$x=-\frac{v}{c}\left(\frac{d^2}{4}+y2\right)^{\frac{1}{2}}.$$

Using the experimental value of v/c, and measuring d and y we find that the "white" fringe is now the hyperbola well over to the left, indicated in Fig. 17(b) by the inclined black line. The

FIG. 19. Interference fringes from two sources, stationary condition; pulse frequency, 30 per second; dark ground illumination giving light deviation perpendicular to line joining sources.

fringe system is skewed in the direction of motion of the medium.

If we introduce the Fitzgerald contraction, d becomes $d[1-v^2/c^2]^{\frac{1}{2}}$, and we measure x as larger by the factor $1/([1-v^2/c^2]^{\frac{1}{2}})$.

We then get for *the exact expression for the aberration of the central fringe,*

$$x=\frac{v}{c}\left[\frac{d^2}{2}+\frac{y^2}{1-v^2/c^2}\right]^{\frac{1}{2}}.$$

When y is large compared to d we have

$$\frac{x}{y}=\tan\epsilon=\frac{v}{c[1-v^2/c^2]^{\frac{1}{2}}}.$$

It may readily be verified that this equation also gives the position of the central fringe from a plane wave front incident on two stationary apertures, separated by the distance d at the angle

$$\sin^{-1}\frac{v}{c}=\tan^{-1}\frac{v}{c[1-v^2/c^2]^{\frac{1}{2}}}.$$

We thus derive the aberration formula from a study of wave interference phenomena without recourse to the concept of rays.

VISIBILITY OF THE INTERFERENCE FRINGES

While the *positions* of the interference fringes remain symmetrical when the medium is in motion with respect to the source, it appears by inspection of Figs. 6 and 7 that the intensities or visibilities of the fringes alter with the motion of the medium. This, however, is a conclusion which must not be accepted without, first, entirely eliminating all known unsymmetrical disturbances introduced by motion, and, second, carefully investigating what the photographs are actually recording, taking into account the conditions of illumination.

As to the first problem, the outstanding recog-

FIG. 20. Interference fringes from two sources; relative speed of sources and medium 16 cm per second ($v/c=0.725$); illumination conditions as in Fig. 19.

nized unsymmetrical phenomenon is the occurrence of the stationary group waves between capillary and gravity waves caused, as, already mentioned, by excessive air pressure in the jets. The unsymmetrical effect shown in Fig. 7 is principally the result of these additional waves, as can be recognized by inspection of Fig. 16. In order to make possible the use of very small pressures, so as to prevent these waves, the method of illumination was radically changed, from the bright ground illumination used in obtaining the photographs thus far shown, to *dark ground illumination.* This was accomplished by placing an obstacle over the center of the camera lens, in place of the previously used small aperture. With no disturbance of the mercury surface it appears black, and, with a small obstacle, a very slight distortion of the surface appears as a bright area, which by sufficient photographic exposure, can be recorded even where the amplitude of the distortion is minute. With this method of illumination the air jet

pressures can be kept below the point where gravity waves appear.

A qualitative consideration of the method of recording the fringes by the light they deviate makes it obvious that the amount of light deviated must be a function of the steepness of face of the constituent fringes. This is illustrated by the ripple pattern from two sources, shown in Fig. 18. This, taken by means of a centrally placed opaque obstacle in the camera lens shows how the narrow ripples on the side from which the medium enters (as indicated by the pointer) furnish much more light than the broad ripples on the other side. The integration of a time exposure, made to show the stationary fringe system, remembering that the same number of ripples pass any point in a given time, would thus be stronger on the slow side. The amplitudes of the waves are thus not represented even approximately by this method of illumination.

In order to establish conditions suitable for showing the relative amplitudes on the two sides of the jets, experiments were made with two

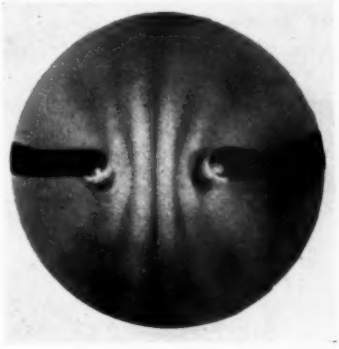

FIG. 21. Same as Fig. 19 except dark ground illumination arranged to deviate light parallel to line joining sources.

different arrangements of dark ground illumination. In both arrangements a narrow occulting strip was used, extending across the whole lens, in place of the small central opening or obstacle previously used. The first experiment was to orient the strip at right angles to the direction of motion of the medium. By so doing the light deviated and made visible is to a predominant degree determined by the steepness of face of the ripples at right angles to the direction of motion of the medium. Figures 19 and 20 show the appearance of the interference fringes for the stationary and moving conditions. It will be seen that the fringes are greatly enhanced on the side from which the medium approaches the source, indicating, in agreement with Fig. 18 that the ripples on this side are narrower and steeper of face than on the other side, but not whether they are of greater or less or equal amplitude.

Next the occulting strip was turned so as to be parallel to the direction of motion of the medium. The appearance of the fringes with this method of illumination is shown in Figs. 21 and 22. In striking contrast to Figs. 19 and 20 these photographs show *the fringes to be identical for the stationary* and *for the moving medium*, despite the extreme distortion of the ripples corresponding to the latter condition as shown in Fig. 18, which was taken with the same large velocity of the medium.

This latter condition of illumination is considered to present the true picture of the relative amplitudes of the wave and fringe systems, fore and aft of the jets. What we have is an integration of the light flashes from the *sides* of the constituent ripples where they flow along the stationary interference minima. The number of flashes passing a given point is the same wherever the point is located, by a well-known characteristic of the Doppler effect; the duration of each flash is directly as the length of (the side) of the ripple and inversely as its velocity, but since the length of the ripple is directly as its velocity (frequency

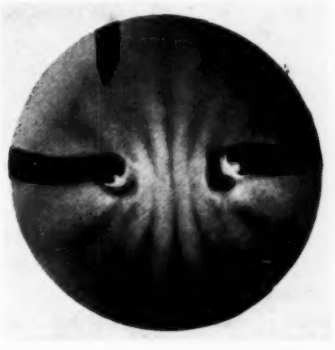

FIG. 22. Same as Fig. 20 except dark ground illumination arranged to deviate light parallel to line joining sources.

being constant), equal integrations of flashes means *equal amplitudes of the ripples*.[4]

How this can come about may be pictured as follows: We have, first of all, as a characteristic of all wave motion that the amplitude falls off directly as the distance traversed *in the medium*. When the medium is in motion the waves originate at distances $d/(1-v/c)$ and $d/(1+v/c)$ from the source, where d is the distance when the medium is stationary. Because of this effect alone we should expect the amplitudes to be less on the side from which the medium enters by the factor $1-v/c$, on the other side greater by the factor $1+v/c$. Consider, however, a train of waves on either side of the source. On one side the train is compressed, on the other expanded. For the same content of medium in a wave to be preserved the amplitude of the shortened waves must increase, and vice versa. This change of amplitude will be inversely proportional to the wave-lengths, the amplitude of a wave on the side from which the medium enters will be $a/(1-v/c)$, or the other side $a/(1+v/c)$. These factors exactly neutralize the changes due to altered distances of travel, leaving the amplitudes in both cases, a, the value for a stationary medium. This variation of amplitude in a train of waves may be likened to the effect of longitudinally stretching or compressing a wire which has been bent to follow a sine curve. The occurrence and character of such an effect here postulated from the experimental result, would in any given mode of wave production, such as electromagnetic radiation, of course have to be established by analysis of the appropriate equations defining the mode of production and propagation of the waves.

The principal interest of this point lies in the corresponding optical case; in the question raised by Fizeau in 1854, whether a system consisting of light source and receiving surfaces equally distant in front and behind, will not permit detection of motion through the ether by variation in the relative intensities of irradiation of the two surfaces. If the amplitudes remain equal fore and aft for the optical case, as they appear to be in our experiment with ripples on mercury, then, according to Poynting's theorem there is a flow of energy into the receiving surfaces of

$$\left(\frac{c\pm v}{c}\right)U_s,$$

where U_s is the energy flow for the system when stationary. The irradiation of the surfaces should therefore differ by an effect of the first order in v/c.

This conclusion is in conflict with the substantially null result of Nordmeyer's experiment[5] in 1903, and with analyses of the problem by H. A. Lorentz[6] and by A. H. Bucherer.[7] According to these analyses the amplitudes fore and aft in a moving system are different by the factors $1/(1\pm v/c)$ from the stationary condition; the intensities by the squares of these factors. In order to compensate for these differences they invoke the work done by radiation pressure against the *absolute* velocities of the surfaces. This compensation is however purchased at the price of requiring the radiation pressure on the receiving surfaces to vary with the velocity of the system by factors of the first order in v/c. (This consequence is not noted by these authors, but follows from their equations.)

It is important to note that a variation of irradiation or of radiation pressure as the first power of v/c, is not subject to compensation by the Fitzgerald contraction or the Larmor-Lorentz frequency change. The latter, as shown elsewhere,[8] makes the different times of arrival of light signals at points equidistant in front of and behind a moving source *read* the same, because of an accumulated difference of setting in the clocks moved to the points of observation. Change of clock setting plays no part in the measurement of radiation or pressure.

The whole problem of radiation and radiation pressure in a moving system needs re-examination. A forthcoming paper by Mr. T. C. Fry contains a resurvey of this problem, leading to conclusions substantially different from those of Lorentz and Bucherer.

[4] Figures 21 and 22 thus supersede Figs. 6 and 7 as faithful representations of the interference system.

[5] Nordmeyer, Ann. d. Physik [5] **11**, 284 (1903).
[6] H. A. Lorentz, Kgl. Akad. d. Wiss. Amst. p. 678 (1902).
[7] A. H. Bucherer, Ann. d. Physik [5] **11**, 270 (1903).
[8] H. E. Ives, J. Opt. Soc. Am. **27**, 267–73 (1937).

Erratum: The Response of Sputtered Thermocouples to Interrupted Radiation

L. HARRIS AND A. C. SCHOLP
Massachusetts Institute of Technology, Cambridge, Massachusetts
(J. Opt. Soc. Am. **30**, 519 (1940))

IN a paper of this title which appeared in the November, 1940, issue, the following corrections should be made:
An addition should be made on page 520 under Eq. (3)

$$V_{\text{a.c.}} = \frac{V_{\text{d.c. converter}}}{2.85} \qquad \text{(see reference 4).}$$

On page 520, Table I, the heading of the third column should read:

$V_{\text{d.c.}}$ converter volts.

In the second column, page 522, under "Sensitivity," the last line of the first paragraph "the sensitivity is 185×10^{-10} watt cm^{-2}" should read: "the sensitivity is 185×10^{-9} watt cm^{-2}." In the same section, the second paragraph, seventh line, "the sensitivity is 2.2×10^{-10} watt," should read: "2.2×10^{-9} watt."

Physicists Needed for National Defense Work

The civil-service examinations announced on November 14, 1940 for physicists have not produced enough applicants. The announcements have been amended by the United States Civil Service Commission to extend the closing dates for receipt of applications for nearly a year—until December 12, 1941. Only one application need now be filed at the Commission's Washington office by persons wishing to apply for two or more positions, and no written test is required for any grade.

The positions to be filled include the following grades: physicist (any specialized branch), $3,800 a year; also principal, $5,600; senior, $4,600; associate, $3,200; and assistant, $2,600 a year. These salaries are subject to a 3½ percent retirement deduction.

Applicants for all grades must have completed a four-year college course; for the three higher grades they must have had major study in physics; and for the two lower grades they must have completed at least 24 semester hours in physics. They must have had professional experience in physics, but partial substitution of graduate study in a specialized branch of physics may be made. Applicants will not be required to report for examination—they will be rated on their qualifications as shown in their applications and on corroborative evidence.

Further information regarding the examination, and the proper application forms, may be obtained from the Secretary of the Board of U. S. Civil Service Examiners at any first- or second-class post office, or from the U. S. Civil Service Commission, Washington, D. C.

Criteria and the Intensity-Epoch Slope

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(Received August 2, 1940)

I. Introduction

In a previous paper,[1] arguments for extending the theory of resolving power to include the intensity-epoch slope as a factor have been presented. That paper, along with another,[2] has laid foundations upon which can be established a theory of optical resolution and resolving power, adequate for the design and use of optical instruments, and consistent with present knowledge of the subject. Before the theory itself can be developed in full, and applied to the assignment of numerical values, it is necessary to consider the persistently vexing problem of criteria for a limit of resolution.

The necessity for a criterion does not disappear on the extended theory, but the meaning of a criterion takes on a new significance. For it is now intimately connected with the manner in which the average value of the intensity-epoch slope is to be taken. Inasmuch as this is so, part of the work which has been done on the subject of criteria will need to be reinterpreted—translated into the language of the modified theory. Another part is apparently unsuited for the purposes of criteria on the new point of view. This latter part seems to be more closely related to another inadequately developed topic in the theory of optical instruments. Somewhat more will be said concerning it in the concluding section of the present paper.

In this paper, various criteria which have been employed for isolated optical problems will be classified, and compared. Their applicability will be discussed, and numerical examples will be used to illustrate the method of using them in connection with the intensity-epoch slope. However, no novel criterion for resolution will be presented, and the considerations upon which the choice of a criterion must be based will not be discussed at length.

[1] B. P. Ramsay, O. T. Koppius and E. L. Cleveland, "The prism and the theory of optical resolution," J. Opt. Soc. Am. **30**, 439 (1940).

[2] E. L. Cleveland, B. P. Ramsay and O. T. Koppius, "Optical resolving power and the photon theory," J. Opt. Soc. Am., forthcoming issue.

II. Classification of Criteria

Let I_1 and I_2 be the intensity functions which describe two distribution patterns whose resolution is desired. Of course, experimental observations can be made upon neither I_1 nor I_2, but upon the composite intensity distribution, J. In a simple case involving the resolution of only these two components,

$$J=I_1+I_2. \tag{1}$$

From this relation, it may be observed that there are three bases which may be used in constructing criteria for a limit of resolution. It is convenient to list them as follows.

Class A.—Criteria of this class specify in radians the separation between I_1' and I_2' at the limit of resolution.[3] In criteria of this sort, the values of I_1^*, I_2^*, and J^* (at the point of overlap) depend entirely upon the form of the intensity function[4] which is appropriate to the given device. Examples of this class which will be noted below are the criterion which Rayleigh called "convenient," and the Schuster criterion for "absolute" resolution.

Class B.—Criteria of this sort employ some property of the composite distribution, J, to define the limit of resolution. Here, the separation of the maxima, and the values of I_1^* and I_2^* are matters of secondary interest. Examples are the generalized Rayleigh criterion, and the "actual" limit of resolution which Sparrow obtains from his undulation condition. The criteria which Ditchburn proposes for his stages of resolution also belong to this class.

Class C.—A third class of criteria defines the limit of resolution in terms of the intensity function, I. In applying a criterion of this sort, one is not directly concerned with the separation

[3] In this paper, primes are used to indicate maximum values, double primes to indicate minimum values, and an asterisk to denote the value of a quantity at the criterion point which is sometimes called the point of overlap.

[4] For a catalog of intensity functions appropriate to various interferential devices, see L. Sturkey and B. P. Ramsay, "A general interferential method." This paper will shortly appear in Phil. Mag.

of the maxima, or with the value of J^*. Examples to be listed are Houston's half-width criterion, and the "less arbitrary" criterion of Buxton. In (25), it will be noted that the generalized Rayleigh criterion can be stated in such a form as to make it a criterion of Class *C*.

III. Criteria for a Limit of Resolution

The criteria which will be noticed here will not be listed in chronological order. The historical development of the concept of criteria is of minor importance. The points of interest are the several bases which have been used for the construction of criteria, the difficulties which successive criteria have tried to obviate, and the difficulties which they have introduced. It is noteworthy that although these criteria are applicable in large measure to objective and spectroscopic resolution alike, they are stated for the most part in terms of spectroscopic resolution. At the same time, it may be observed that the development of the concept of criteria roughly corresponds to the classes *A*, *B*, and *C* in the order named.

(a) The Rayleigh criterion

The Rayleigh criterion is based upon the form of the intensity pattern produced by a prism or grating spectroscope which is illuminated by perfectly monochromatic light. If light of two wave-lengths is received by the spectroscope, each wave-length produces its own intensity pattern. What is observed, either visually or photographically, is the sum of the overlapping intensities due to the two patterns. Rayleigh observed that two spectral lines can just be separated visually when the central maximum of wave-length λ falls on the first minimum of wave-length $\lambda+\Delta\lambda$. This he considered to be "the limit of closeness at which there could be any decided appearance of resolution." When produced by a prism spectroscope, the intensity pattern of either line individually is given by

$$I=I'(\sin^2\alpha)/\alpha^2. \tag{2}$$

The composite pattern of the two lines, equal in intensity and separated by an amount $2b$, is given by

$$J=I'\left\{\frac{\sin^2(x-b)}{(x-b)^2}+\frac{\sin^2(x+b)}{(x+b)^2}\right\}. \tag{3}$$

Here x is the variable in terms of which the composite intensity distribution is described. Its origin is a point midway between the two principal maxima. The intensity distribution of each of the lines, as well as that of the composite pattern, is shown in Fig. 1. It may be observed from (3) that the two lines are just resolved, according to the Rayleigh criterion, when the separation of the maxima has the positive value

$$\phi=2b=\pi. \tag{4}$$

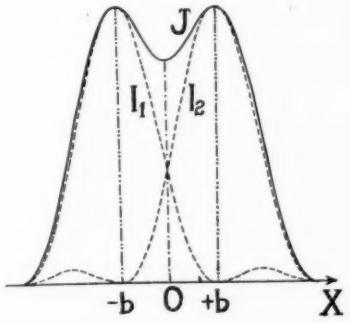

Fig. 1. Diagram to show the application of the Rayleigh criterion to the prism distribution functions. I_1 and I_2 are the intensity curves, J is the composite curve, x is the parameter in terms of which the distribution is described, and b is the criterion value. The limit of resolution is $2b$.

Of this criterion, Rayleigh said, "This rule is convenient on account of its simplicity and it is sufficiently accurate in view of the necessary uncertainty as to what exactly is meant by resolution."

(b) The Schuster criterion

It may be seen from Fig. 1 that the resolution specified by (4) is not absolute;[5] it appears merely as a dip in the J distribution curve. Schuster remarked[6] that visual resolution is a physiological phenomenon, and that with a photograph or a bolometer the test of resolution is different. "It would therefore have been better not to have called a double line 'resolved' until the two images stand so far apart that no portion of the central band of one overlaps the central band of the other, as this is a condition which applies equally to all methods of observa-

[5] W. E. Williams, *Applications of Interferometry* (E. P. Dutton and Company, 1930), p. 79.

[6] A. Schuster, *Theory of Optics* (E. Arnold and Company, 1924), p. 158.

tion." This criterion defines a limit of resolution twice that of the Rayleigh value. It gives for the separation of the maxima at the limit of resolution

$$\phi = 2b = 2\pi. \tag{5}$$

This relation specifies the value of b to be used in (3). From Fig. 1, it may be seen that in a separation of this amount the secondary maxima of the component patterns would produce a noticeable effect on the composite distribution. Moreover, as Williams emphasizes, dips much smaller even than that obtained with the Rayleigh criterion can be accurately measured with modern microphotometers.

(c) The generalized Rayleigh criterion

It should be noted that in the forms given, criteria such as those listed in (4) and (5) are applicable only to instruments having an intensity function of the form (2). For instruments such as an absorbing prism or a Fabry-Perot interferometer, this type of criterion ceases to be applicable.[7] The Rayleigh criterion has been generalized in such a way, however, as to make it available for all problems of optical resolution. It may be observed from (3) and (4) that at the point $x=0$, the intensity value of the composite curve is

$$J'' = I'(4/\pi^2 + 4/\pi^2). \tag{6}$$

Thus it follows that the ratio of J'', the central minimum of the composite curve, to either maximum, $J'=I'$, is

$$J''/J' = 8/\pi^2 = 0.810. \tag{7}$$

This relation may be used as the basis for a generalized criterion which may be stated as follows: Any two lines are resolved if the ratio J''/J' is not greater than 0.810. In this form, the criterion is applicable to all types of optical instruments, including the absorbing prism[8] and the Fabry-Perot interferometer[5] as well as devices for which the simple Rayleigh criterion is serviceable. In this form, the criterion has lost all semblance of analytical significance; the choice of the ratio value 0.810 is wholly optional. Sparrow points out that the relative merit of different instruments, which the criterion is designed to measure, varies with the choice of the ratio value. To illustrate, he considers a grating and a Fabry-Perot interferometer which have the same limit of resolution on the basis of this criterion. Then, it may be observed that if the right-hand member of (7) were 0.90, the interferometer would be superior; but if the ratio were 0.70, the grating would be superior.

(d) The Sparrow undulation condition

Sparrow observes that the only fair basis upon which different instruments can be compared must depend upon "an actual limit of resolution." As the angular separation is gradually decreased from that specified by the Rayleigh criterion, the central minimum becomes gradually shallower, until finally it disappears. Sparrow declares that this disappearance of the central minimum is the criterion which gives the "actual limit of resolution." This condition, which he calls the "undulation condition," is described by

$$\partial^2 J/\partial x^2 = 0 \quad \text{at} \quad x=0. \tag{8}$$

The differentiation of (3), required by (8), yields an expression which is not easily solved for b; but a solution by successive approximations readily leads to the value

$$\phi = 2b = 2.606. \tag{9}$$

By comparison of (4) and (9), it appears that the resolving power of a prism spectroscope is approximately twenty percent higher according to Sparrow's criterion than according to the more convenient Rayleigh criterion. Thus for a transparent prism of thickness T and refractive index μ, the resolving power according to Sparrow's criterion is

$$\rho_s = (-\pi/2.606)T(d\mu/d\lambda)$$

or

$$\rho_s = -1.206T(d\mu/d\lambda). \tag{10}$$

Likewise, for a perfect grating of k lines used in the order m, the resolving power becomes

$$\rho_s = 1.206km. \tag{11}$$

This increased resolving power corresponds, of course, to a decreased limit of resolution. Concerning it, Sparrow says: "The surprising fact is that this limit is *apparently actually attained*, and that the doublet still appears

[7] C. M. Sparrow, Astrophys. J. **44**, 76–86 (1916).
[8] F. L. O. Wadsworth, Phil. Mag. **5**, 355–374 (1903).

resolved, the effect of contrast so intensifying the edges that the eye supplies a minimum where none exists. The effect is observable with both positives and negatives, as well as by direct vision. . . . A very slight diminution of the separation rounds the top of the intensity curve so that there is no resolution; the undulation condition thus defines the limit of resolution quite sharply." Not only Sparrow, but several other observers[9] report that a limit of resolution approximately twenty percent smaller than Rayleigh's is usually obtained.

Rayleigh did not consider the problem of resolving lines of different intensities, except to remark that "something probably depends on the relative intensities of the two components." Sparrow's criterion, however, is applicable to unsymmetrical doublets when the ratio of their intensities is as great as 10 : 3. Moreover, the undulation condition gives a limit of resolution for all cases in which the intensity pattern is modified by finite slit width, or by a decrease in the geometric progression of the intensities of the interfering beams, whether due to absorption or to loss of light by reflection.

One conspicuous difficulty with Sparrow's criterion is that before the limit of resolution can be known, both the relative intensities of the lines to be resolved and the equation of the J curve must be known. In general, this information is not available; and even if it were, the solution of (8) for $2b$ might not be possible in all cases. Reference to Fig. 1 shows that the positions of J' do not correspond to those of I' when a limit smaller than (4) is used. These may be some of the reasons for the fact that the Sparrow criterion is not the last word on the subject. Nevertheless, it is surprising that references to this thoughtful consideration of the subject have not been noted.

(e) Ditchburn's degrees of resolution

In an attempt to define the meaning of resolution more closely, Ditchburn[10] recognizes three stages as important: (α) detection of inhomogeneity, (β) partial resolution, and (γ) complete resolution. The first stage is reached when it can be definitely said that the radiation is nonhomogeneous; the second stage is reached when the observer is able to distinguish the number of components and to get a fairly good idea of their wave-length separation (say, to within ten percent) and a rough idea of their relative intensities.

Ditchburn's conclusions may be summarized as follows:

For the microphotometer.—(α) Inhomogeneity can be detected when the half-width of the microphotometer trace has been increased by about ten percent, provided a standard is available. (β) Partial resolution is obtained with a twenty-percent dip. (γ) Complete resolution is obtained with a sixty-percent dip.

For the eye.—(α) Inhomogeneity can be detected just before the maximum divides. (β) Partial resolution is obtained with about a forty-percent dip. (γ) Complete resolution is obtained with about a sixty-to-seventy-percent dip.

It appears that for both the eye and the microphotometer the Rayleigh criterion corresponds roughly to Ditchburn's "partial resolution" stage, whereas the undulation condition gives a resolution that resembles his "detection of inhomogeneity."

(f) The Houston criterion

Houston[11] has used a half-width criterion, according to which two purely monochromatic lines of equal intensity are just resolved when the separation of their maxima equals the width of the intensity pattern of either line where its intensity has dropped to one-half its maximum value. For the prism, this gives a value for ϕ less than the value (4) given by the Rayleigh criterion. The significant point about this criterion, however, is that it is not based upon the absolute value of ϕ, nor upon properties of the J distribution curve. It merely requires that the I curves intersect at points where $I^* = I'/2$. The criterion is appealing because of the theoretical significance of the half-width of a spectrum line in other regards.

(g) The Buxton amplitude criterion

Buxton[12] has proposed a criterion of the same class as that used by Houston. Instead of using

[9] T. Preston, *Theory of Light*, fifth edition (Macmillan and Company, 1928), p. 266.

[10] R. W. Ditchburn, Proc. Roy. Irish Acad. **39**, 58–72 (1930).

[11] W. V. Houston, Phys. Rev. **29**, 480 (1927).

[12] A. Buxton, Phil. Mag. **23**, 440–442 (1937).

the intersection of the intensity curves for his criterion, he prefers to use the intersection of the amplitude curves. The amplitude function may be taken as the square root of the intensity function. Thus it may be noted that somewhere between the maximum and minimum of the amplitude curve, its curvature changes sign. The criterion which Buxton suggests is that at the limit of resolution the amplitude curves should intersect at their points of inflection. This criterion is illustrated by applying it to the objective resolution of a telescope.

The intensity function for the telescope is usually expressed in terms of the Bessel function, $J_1(z)$, as

$$I=\left\{\frac{2}{z}J_1(z)\right\}^2, \tag{12}$$

where

$$z=2\pi R y_1/\lambda f. \tag{13}$$

Here R is the radius of the circular aperture, f is the focal length of the telescope objective, λ is the wave-length, y_1 is the distance of the point at which the intensity is taken from the center of the "spurious disk," and $J_1(z)$ is the Bessel function of the first kind of order one. Then the point of inflection in the amplitude curve occurs where

$$\frac{d^2}{dz^2}\left\{\frac{J_1(z)}{z}\right\}=0. \tag{14}$$

Execution of the differentiation and use of recursion formulas yields

$$J_1(z)\left\{\frac{2}{z}-\frac{z}{3}\right\}=J_0(z). \tag{15}$$

From tables it may be seen that (15) is satisfied if $z=2.30$. Thus by the Buxton criterion, the angular separation at the limit of resolution is

$$\phi_B=2b=2y_1/f \tag{16}$$

or

$$\phi_B=4.60\lambda/2\pi R=1.46\lambda/2R. \tag{17}$$

The corresponding limit of resolution derived from the convenient Rayleigh criterion is

$$\phi_R=3.83\lambda/2\pi R=1.2197\lambda/2R. \tag{18}$$

The choice of the amplitude curve instead of the intensity curve simplifies the calculation in the illustration which Buxton has chosen, but this is not generally true. It is noteworthy that although the amplitude curve may seem somewhat more fictitious than the intensity curve, neither of these—but rather the J curve—is involved in experimental measurements of resolution. Indeed, Buxton regards his rule as "a less arbitrary criterion" than Rayleigh's. For reasons noted in discussing the Rayleigh criterion, Buxton's criterion is applicable to intensity functions for which the latter is not suitable.

IV. The Single-Line Theory of Resolving Power

Further reflection on these several criteria reveals that the properties of a single line are sufficient to define a criterion of resolution.[13] For, indeed, that is exactly what is done by the criteria of Class A and Class C. For they define criteria either in terms of $b=\Delta\alpha$, a certain change in epoch value of a single maximum, or in terms of ΔI, a certain requisite change in intensity value of this single maximum.

In a previous paper,[1] it has been shown that the average value of the intensity-epoch slope, $\Delta I/\Delta\alpha$, is an important factor of optical resolving power. From this point of view, a criterion serves the sole purpose of specifying the interval over which this average value is to be taken. Since the relation between I and α is given by the intensity function,[5] the value of both ΔI and $\Delta\alpha$ are given whenever either is specified by a criterion. Mathematically, the distinction between criteria of Class A and those of Class C is merely the choice as to whether I or α is to be taken as the independent variable. In Class A, α is chosen as the independent variable; this makes it necessary to assign arbitrary values to $\Delta\alpha$. But in Class C, it is I which is taken as the independent variable, and ΔI to which arbitrary values are assigned.

In the former paper,[1] simple examples of the intensity-epoch slope have been mentioned without involving the concept of criteria. It was the Schuster criterion which was used there. For a prism, it gives by (5)

$$\Delta\alpha=b=\pi$$
$$\Delta I=1$$

[13] R. W. Ditchburn and E. J. Power-Steele, Proc. Roy. Irish Acad. **41**, 137–149 (1933).

and

$$\Delta I/\Delta\alpha = 1/\pi. \tag{19}$$

For a multiple beam device, such as a grating of k rulings, the Schuster criterion gives

$$\Delta\alpha = \pi/k, \quad \Delta I = 1 \tag{20}$$

and

$$\Delta I/\Delta\alpha = k/\pi. \tag{21}$$

The application of the Rayleigh criterion to the prism gives

$$\Delta\alpha = b = \pi/2, \tag{22}$$

according to (4), and

$$\Delta I = (1 - 4/\pi^2), \tag{23}$$

as may be seen from (6). Thus the Rayleigh criterion gives

$$\frac{\Delta I}{\Delta\alpha} = \frac{(1-0.405)}{\pi/2} = \frac{1.19}{\pi}. \tag{24}$$

Other criteria could be applied to numerical examples of this sort. Thus for Houston's half-width criterion, $\Delta I = 0.5$.

It is interesting to note that the generalized Rayleigh criterion may become a criterion of Class C. This is the effect of stating it in the form

$$\Delta I = (1 - 4/\pi^2). \tag{25}$$

The use of this criterion will be illustrated by applying it to the Fabry-Perot interferometer.

The intensity function which is germane to the Fabry-Perot interferometer is the one which has been called[5] the finesse distribution. It is

$$I_f = I'/(1 + F \sin^2 \alpha), \tag{26}$$

where I' is the maximum which occurs when α has the value

$$\alpha' = m'\pi. \tag{27}$$

If $I' = 1$, as has been assumed in the examples above, the value of I at the lower limit set by the criterion (25) is $I^* = 0.405$. Let α^* be the value of α corresponding to I^*. Then,

$$I^* = 0.405 = 1/(1 + F \sin^2 \alpha^*), \tag{28}$$

$$\sin^2 \alpha^* = (1 - 0.405)/0.405F, \tag{29}$$

$$\alpha^* = m'\pi + \sin^{-1} (1.469/F)^{\frac{1}{2}}, \tag{30}$$

$$\Delta\alpha = \alpha' - \alpha^* = \sin^{-1} (1.21/F^{\frac{1}{2}}). \tag{31}$$

Thus from (25) and (31),

$$\frac{\Delta I}{\Delta\alpha} = \frac{(1-0.405)}{\sin^{-1} (1.21/F^{\frac{1}{2}})}. \tag{32}$$

In this expression, F is the coefficient of finesse[14] given by

$$F = 4R/(1-R)^2, \tag{33}$$

where R is the intensity coefficient of reflection.[15] Thus it may be seen that for $R = 0.9$, $F = 360$. This means that the angle in the denominator of (32) is so small that it may be replaced by its sine. Hence,

$$\Delta I/\Delta\alpha = 0.595F^{\frac{1}{2}}/1.21, \tag{34}$$

or

$$\Delta I/\Delta\alpha = 1.19R^{\frac{1}{2}}/1.21(1-R), \tag{35}$$

when (33) is substituted in (34).

For the sake of comparisons, it is desirable to write (35) in the form

$$\frac{\Delta I}{\Delta\alpha} = \frac{1.19}{\pi}\left[\frac{\pi}{1.21}\frac{R^{\frac{1}{2}}}{(1-R)}\right]. \tag{36}$$

In this equation, the quantity in brackets is the factor which Williams[5] has called the *effective number of reflections*, N. On the other hand, the factor $1.19/\pi$ is a coefficient which is characteristic of the generalized Rayleigh criterion (25), as may be seen by its application to the prism. The result is given by (24). Similarly, the intensity-epoch slope for multiple beam devices is

$$\Delta I/\Delta\alpha = (1.19/\pi)k, \tag{37}$$

instead of the value (21) which follows from the Schuster criterion. Thus, comparison of the number of beams, k, in (37) with the bracketed factor in (36) suggests the usefulness here also of the analogy suggested by Williams:

$$N = \left[\frac{\pi}{1.21}\frac{R^{\frac{1}{2}}}{(1-R)}\right]. \tag{38}$$

[14] C. Fabry, *Les Applications des Interferences Lumineuses* (Rev. d'optique, 1923), pp. 28–29.

[15] In the mathematical development, R appears as the geometric ratio of the amplitudes of the compatible beams whose superposition produces the intensity function (26). Its physical significance appears on applying the Stokes amplitude coefficient of reflection (sometimes called the reflecting power) to the incident beam at each reflection. Then, since internal reflections in the interferometer occur in pairs, the amplitude of each emerging beam is the product of the amplitude of the incident beam by some integral power of the square of the Stokes coefficient; and this square is the intensity coefficient, R.

In a later paper, it will be shown that this analogy persists in another regard.

The examples above sufficiently demonstrate the intimate relation between the criterion value and the intensity-epoch slope. They also illustrate the method of finding the intensity-epoch slope for any criterion that may be chosen, and for any sort of optical device whose intensity function is known. Nevertheless, two observations may be listed as rules to be observed in order to avoid errors in applying this procedure.

The first is that the unit in which the criterion value, ΔI, is to be measured is I', the maximum of the intensity distribution to which it is applied.

In the second place, it may be noted that care must be exercised in the choice of the epoch function with respect to which the slope is to be measured. The difficulty may be illustrated by writing the finesse intensity function (26) in the simple form,[16]

$$I_f = Z^2/(1+R^2-2R\cos\gamma). \tag{39}$$

This expression can be seen to be identical with (26) by introducing the coefficient of finesse (33), and using the relations

$$I' = Z^2/(1-R)^2 \tag{40}$$

and

$$\alpha = \gamma/2. \tag{41}$$

It is apparent that the intensity-epoch slope could be expressed either as $\Delta I/\Delta\alpha$ or as $\Delta I/\Delta\gamma$. The only requirement here is that of consistency, so that comparisons of optical instruments based upon the results may be significant. Confusion in particular cases may be dispelled by referring the given intensity equations to the generic intensity function[4] which is applicable to all interferential devices.

V. Criteria of Class *B*

An attempt to summarize the subject suggests that there may be some value in distinguishing between the theory of resolving power and the theory of optical resolution. For there are two matters with which the inventors of criteria have been interested—(a) the comparison of optical instruments which may be used for a given purpose, and (b) the use of a given instrument to effect the purposes for which it may be employed. In the first case, the theory is concerned with the design of optical systems. For instance, is it desirable in an echelon of given dimensions to have relatively few laminae of large order, or a greater number of laminae of correspondingly smaller order? A theory of resolving power must offer a basis for comparing these two cases. It might clarify the study of resolving power to define it as the treatment of problems of this sort.

In the second place, the theory is interested in how the resolution which is effected in a given case will be revealed—or, conversely, how the resolution which has been experimentally observed is to be interpreted. Suppose one knows that his spectroscope will resolve a given doublet whose components are equal in intensity. What value does this information have in indicating what one may expect of this spectroscope in resolving another pair of components whose intensity ratio—as predicted by some theory of spectra—is expected to be 10 : 4? Is the prediction of the spectral theory confirmed if one obtains a ten-percent broadening of the line, or must one expect a ten-percent dip? Or more generally, how can one obtain from a complex intensity pattern the number, the difference in wave-length, and the relative intensity of the components? If solutions to problems of this sort were called theories of resolution, one could remark that resolving power is only one of the factors upon which resolution depends.

In this sense, Michelson's visibility studies[17] were an experimental and theoretical adventure in the subject of resolution. It is desirable that the theory of optical instruments be developed further in this direction. This is emphasized by such work as that of Williams and Gibbs[18] in emphasizing the necessity for distinguishing between the maximum of a line (i.e., J' of the composite curve) and its center of gravity (i.e.,

[16] C. Fabry, *Optique* (Les Presses Universitaires de France, 1934), 70.

[17] A. A. Michelson, Phil. Mag. (5) **31**, 338 (1891); **34**, 280 (1892).

[18] R. C. Williams and R. C. Gibbs, Phys. Rev. **45**, 475 (1934); **45**, 491 (1934).

I' of the intensity function). It is in this regard that the study of Class B criteria—such work as that of Sparrow and Ditchburn—is of prime importance. For "resolution" is concerned with the form of the composite curve which results from objects or lines of different intensity and separation, and with the interpretation of such curves when they have been experimentally observed. It is therefore primarily a study of the J distribution curve.

On the other hand, the I distribution curve appears to be the most satisfactory basis for a theory of resolving power in the restricted sense mentioned above.

Commercial Standards for Laminated Lenses for Sun Glasses

THE recommended commercial standards for laminated lenses for sun glasses, reviewed on page 331 of the August, 1940, issue of the *Journal of the Optical Society of America*, have been incorporated with previous similar commercial standards for all-glass lenses. These new specifications are designated as "Ground-and-polished lenses for sun glasses (second edition), commercial standard CS78-40," and "Blown, drawn, and dropped lenses for sun glasses (second edition), commercial standard CS79-40." Copies of these standards will be obtainable from the United States Government Printing Office, Washington, D. C.

Chemical Methods for Increasing the Transparency of Glass Surfaces

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THE amount of light transmitted by a lens or prism can be increased by suitable chemical treatment of the polished glass surface. The phenomenon was first discovered by Taylor[1] in England. The improvement produced by treatment was described by Kollmorgen[2] in 1916. Wright[3] in 1921 told of experimental work at the Bausch and Lomb Optical Company plant during the war period.

The chemical treatment involves the formation of a transparent surface film of low refractive index by selective solution of some of the elements present in the glass. Such removal is possible without damage to the surface polish if the solvent does not attack silica.

The large scale use of chemical processes for increasing the light transmission of optical systems was delayed by a lack of knowledge of the physical and chemical principles involved. Buyers refused to accept lenses if the surfaces showed interference colors. The recent publications of Strong,[4] Blodgett,[5] Cartwright and Turner[6] have not only made clear the relationships between film thickness, color, reflectivity, and light transmission, but have also resulted in a demand for the improved lens systems that can be made when surface reflections are decreased. Blodgett[5] has determined that the surface layer formed by acid leaching of a lead glass has a refractive index equal to that of fused silica. The chemical analysis of leached glass would indicate that pure SiO_2 is seldom formed, but the optical characteristics of treated glasses can be calculated in close agreement with experimental values if the film is assumed to have the properties of silica.

Films Formed by Weathering

The Bausch and Lomb Fellowship at Mellon Institute in 1936 started a research program on the chemical and physical properties of glass surfaces. The study of silica surface films began as one phase of the investigation of the durability of optical glass. Glasses containing large amounts of lead or barium may acquire surface films in use if the surface comes in contact with water. Thin films are harmless, but methods of preventing their accidental formation were studied. Sufficient data were collected so that methods for preparing films of controlled thickness were available when the demand for lens systems with low surface reflectivity developed.

Physical Properties of Silica Films Produced by Chemical Treatment of Glass

The optical theory and the mathematical relationships involved in the lowering of surface reflection losses by thin surface films have been thoroughly covered by Blodgett.[5] A lens that has been chemically treated to remove materials other than silica from the surface layer does not differ visibly from an untreated lens except for the interference color that is seen when white light is reflected from the surface. The color is governed by the thickness of the surface layer. A lens that is treated to obtain the maximum transparency for white light will appear purple. The surface layer does not differ noticeably from the base glass in hardness or scratch resistance. A lens that has been formed to a specific surface curvature before treatment will pass the same test glass inspection for accuracy of curve after treatment. If the treatment is applied to half of a lens surface the boundary line may produce a barely visible shift in the interference figure seen on test glass inspection.

The gain in light transmission produced by a surface film of the correct thickness is equal to the decrease in light reflected by the surface. Using a Mazda lamp as a light source and a

* Bausch and Lomb Optical Company's Industrial Fellowship, Mellon Institute, Pittsburgh, Pennsylvania.

[1] H. D. Taylor, *The Adjustment and Testing of Telescope Objectives*. (York, England, 1896).

[2] F. Kollmorgen, Trans. Soc. Ill. Eng. **11**, 220 (1916).

[3] F. E. Wright, Ordnance Dept. Document No. 2037, 76–77 (1921).

[4] J. Strong, J. Opt. Soc. Am. **26**, 73 (1936).

[5] K. B. Blodgett, Phys. Rev. **55**, 391–404 (1939).

[6] C. H. Cartwright and A. F. Turner, Phys. Rev. **55**, 675(A) (1940).

Martens type visual photometer, a sheet of lead glass with a refractive index of 1.72 was found to transmit 86 percent of the light striking the sheet normal to the surface. After formation of a purple surface layer by treatment with an acid solution the light transmission was 97 percent. A light barium crown glass with a refractive index of 1.57 will change from 90 percent to 95.5 percent and a boro-silicate glass with a refractive index of 1.52 will change from 92 percent to 95 percent on treatment. The light lost by surface reflection is thus reduced to approximately one-fifth of the original value for a high refractive index glass and to three-fourths of the original value for a low refractive index glass.

The gain in light transmission is somewhat less than that produced by films of materials lower in refractive index than silica. When the greatest possible gain in transmission is required, evaporated films of low refractive index minerals are preferable; but when hardness and durability are required, the films produced by chemical treatment are superior.

Chemical Processes Involved in Film Formation

Solvents that will remove higher refractive index materials from a glass surface include acid solutions, salt solutions, water, alkaline phosphate solutions, and fused salts. The common glasses are made up of a random network of strongly bonded silicon and oxygen atoms with other elements joined to the basic network through oxygen linkages. The formation of surface layers on the glass is possible because the less strongly bonded elements can enter into chemical reactions without damage to the silica network. When a barium, lead, or borosilicate glass is treated with a water solution of an acid, the barium, lead, or boron atoms leave the glass to go into solution, while hydrogen ions, in some cases at least, replace the metal ions forming a partially hydrated silica layer. When a glass is treated with a salt solution, the reaction may be similar to that produced by a dilute acid, or, under special conditions, metal ions from the salt may enter the glass. When a fused salt is brought in contact with a glass surface, the salt ions may or may not replace metals in the glass depending on the compositions involved and the conditions of the experiment. In producing silica films for increased light transmission, the dilute acid treatment is ordinarily used, since the slight hydration produced has little effect on the refractive index or hardness of the silica film. Glasses containing only alkali, lime, and silica react so slowly with acids that they are not suitable for the treatment here described.

Effect of Solution Composition on the Rate of Film Formation

The common strong acids differ only slightly in the rate at which they will produce a silica film on glass. Nitric acid is preferable to sulfuric acid or hydrochloric acid because of the solubility of its salts. The concentration of the acid has only a slight effect on the rate of film formation. A dilute solution such as 1 percent nitric acid does not produce objectionable fumes and is not dangerous to handle. Weaker acids such as phosphoric acid, acetic acid, or boric acid are slower in their action and are particularly suitable for treating dense barium crown glasses that react too quickly with nitric acid for good control. The weaker acids, however, are sensitive to the effect of materials dissolved from the glass so that the reactivity of the solution decreases with use.

Time and Film Thickness

Berger[7] investigated the rate of film formation with nitric acid at a constant temperature and found that the thickness of the film can be related to the time of treatment by the equation

$$100t = ax + bx^2$$

in which t is the time in hours, x is the film thickness in microns, a is a constant depending on the initial rate of reaction, and b is a constant depending on the protective effect of the film produced. For some glasses such as the dense barium crown types, the constant b is so small that it can be disregarded and the thickness of the film is proportional to the time of treatment. With the borosilicate glasses and the soda, lime silica glasses, on the other hand, the initial rate of

[7] Edwin Berger, J. Soc. Glass Tech. **20**, 257–278 (1936).

attack is fast, but even a thin film greatly reduces the rate of solution.

Temperature and Rate of Film Formation

The temperature at which a glass is treated has an important effect on the rate at which a minimum reflectance film is produced. Roughly, the rate doubles for each 10 degrees C rise in temperature. The change in reaction speed with change in temperature is similar to that of most chemical reactions in that it follows the Arrhenius law, and that when the logarithm of the time required for the reaction is plotted against the reciprocal of the absolute temperature, the points fall along a straight line. In Fig. 1, curve No. 1 shows this relationship between the time required for a minimum reflecting film to form and the reciprocal of the absolute temperature. The curves for different glasses have approximately the same slope so that the time required for treatment at any temperature can be estimated if the time required at one temperature is known. Since a change of 1 degree C may cause a 10 percent change in the speed of film formation, the temperature of the treating solution must be carefully controlled. Large work must be brought to the same temperature as the bath in which it is to be treated if the process is operated on a time schedule.

Modification of the Protective Effect of the Silica Film

The initial rate of reaction between a clean glass surface and an acid solution is governed by the composition of the glass, the composition of the solution, and the temperature. Even with these variables under control, it is seldom possible to treat a lens taken directly from stock and obtain a film of uniform thickness on the two surfaces. In some cases an assortment of mysterious marks and fingerprints appear in different colors. This variation is not found with surfaces treated immediately as they are removed from the polishing machine. The variability is possible because the protective action of the silica film can be modified enormously by dehydration or by baking. Accidental formation of extremely thin silica films from contact with water or from fingerprints is likely when the more soluble

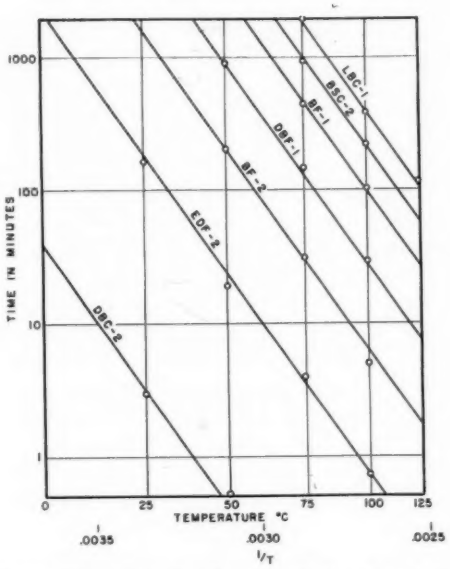

Fig. 1. Time required to form purple film. Log of time plotted against $1/T$.

glasses are handled in the process of manufacture. Operations such as the blocking of a finished surface in pitch for the grinding and polishing of the second surface or heating when the lens is mounted for centering will cause a shrinkage and densification of the silica film so that it is less penetrable to acid action. A glass that can be treated for minimum reflectivity in two minutes when freshly surfaced may require 30 hours for treatment if acid treated for a few seconds and then heated before being replaced in the solution. If a surface is partially filmed but is not heated before it is intentionally treated with acid, it may reach minimum reflectivity more quickly than a freshly prepared surface. Since very thin films do not show interference colors, visual inspection will not indicate whether a lens will react evenly to chemical treatment. For the best results, it is necessary that finished lens surfaces should be handled in such a manner that silica films are not accidentally formed on surfaces to be chemically treated.

Use of Modified Silica Films to Increase Glass Durability

The dense barium glasses and dense lead glasses are sufficiently reactive that a silica film

manufactured to have the correct thickness for minimum reflectivity may increase in thickness if exposed to contact with water containing dissolved carbon dioxide or to the acid applied by a fingerprint. If the lens is baked, however, after the acid treatment, the silica film becomes so stable that no ordinary exposure to weathering will produce an increase in the film thickness. There is a slight shrinkage of the surface layer during baking so that a lens treated in acid just long enough to reach minimum reflectivity will have too thin a layer after baking. A lens that has been treated for a slightly longer time will yield a film of the correct thickness on heating. It is thus possible to select process conditions to yield a stabilized surface with maximum light transmission. The decreased solubility can also be produced by silica films too thin to show interference colors.

Thick silica films are not ordinarily desirable. If a film is made several wave-lengths of light in thickness, it may have sufficient strength so that on dehydration or heating the silica layer will crack and break away from the underlying glass. The danger is greatest with glasses containing only a small amount of silica.

Conclusion

Valuable increases in the light transmission of optical systems can be produced by suitable chemical treatment to form low refractive index surface films. By following the chemical treatment with a baking operation, the durability of the glass surface can be greatly increased.

Proceedings of the Eighth Summer Conference on Spectroscopy and Its Applications

DURING a three-day period in each July of the past eight years, a conference on Spectroscopy and Its Applications has been held in the George Eastman Research Laboratories of the Massachusetts Institute of Technology. At each conference about thirty twenty-minute papers were presented, each followed by discussion periods averaging ten minutes in duration.

The Proceedings of the first four of these conferences were not published. Those of the fifth, sixth, and seventh conferences were published by the Technology Press in booklet form, and are sold by John Wiley & Sons, New York City. The Proceedings of the Eighth Conference, held on July 15, 16 and 17, 1940, are being published in this Journal. A group of nine of the papers is to be found in the present issue. The remainder will appear at an early date.

The Editors are glad to take this opportunity of welcoming to the pages of the Journal a new group of contributors—the authors of papers on spectrochemical analysis. Entirely apart from the Proceedings of the Spectroscopy Conferences, an increasing number of papers on spectroscopy and its applications will be presented, in accordance with the new Journal policy of extending its coverage of all scientific fields dependent on optics.

The scope of the Journal is thus being expanded in what, it is hoped, will prove a virtuous circle. Wider coverage of important fields should result in a more interesting and useful Journal, which in turn should enlarge the circle of readers, subscribers, and Optical Society members. This in turn will make possible still further expansion and improvement of the Journal.

The papers presented at the Eighth Conference on Spectroscopy cover a wide range of subjects. This is to be expected because spectroscopy is of such importance to chemists, biologists, metallurgists, and other scientists, as well as to physicists.

The Editors believe that all branches of science will benefit by the publication of optical papers of varied types in one journal. Science is becoming, of necessity, so specialized that any unifying agency, such as mutual interest in a common tool, deserves employment to the utmost.

Notes on the Physical Basis for Spectrographic Analysis*

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DURING the past two decades there have been phenomenal advances in atomic theory and interpretation of spectra, and simultaneously there has been a remarkable revival of interest in the practical use of spectra for chemical analysis. But the two activities developed independently, and had practically nothing in common until recently. The former was purely scientific, the latter almost entirely empirical. In this period more than 1000 papers on spectrochemical analysis have been published[1] but very few deal specifically or adequately with physical principles fundamental to the art. Empirical development resulted in many variations of apparatus, extensive modification and invention of "methods," and some differences of opinion on certain questions. For example: Should prism or grating spectrographs be used? Should the light source be a flame, an arc, or a spark? Should the material to be analyzed be in the form of solid or solution? Which lines are the most persistent? What factors govern absolute sensitivity? Why are some elements extremely sensitive and others relatively insensitive? Is it really possible to examine any sample for the presence of 70 elements? Scientific answers to these questions are to be found in optical properties of spectrographs, physical characteristics of light sources, and in the mechanism of atomic radiation. The question of "prism *versus* grating"[2] has been discussed in previous conferences and something has been said also about "spark *versus* arc."[3] Without contracting to answer all the remaining questions, I was persuaded to submit a progress report on investigations dealing with the physical basis of spectrographic analysis. With no intention of exhausting this subject, I undertake to discuss it briefly in the most elementary terms.

The main function of a light source for spectrochemical analysis is to vaporize samples and excite the atoms to radiate their characteristic spectra. It is quite generally believed that atomic radiation occurs as a result of transitions between quantized energy states associated with various orbital and spin momenta of the valence electrons. Atoms may be energized (1) by collision with other atoms, molecules or ions (thermal excitation), (2) by impact of energized electrons (electrical excitation) or (3) by absorption of light quanta (optical excitation).

The light sources commonly used in spectrochemical analysis are flames, arcs and sparks. In these sources at ordinary atmospheric pressure it is now quite certain that thermal excitation is the chief factor in the production of spectra. The temperature of a Bunsen flame is approximately 2000°K, and of the oxyacetylene flame about 3000°K. Temperatures of metal arc cores range from 4000 to 7000°K, and the gases and vapors in spark discharges probably have still higher temperatures. Indeed, the temperature which produces the Cu XIX spectrum (characteristic of 29 Cu with 18 electrons removed), has been estimated to be several million degrees.[4] High temperature is necessary for ionization in sources at atmospheric pressure because only at very low pressures is the free path of electrons great enough to permit ionization by impact throughout the volume of the source.

Although Bunsen (and other) flames are classical light sources of spectrographic chemists[5] there is a growing trend to abandon them in favor of electric arcs and sparks. Only 25

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940.

[1] W. F. Meggers and B. F. Scribner, "Index to the literature on spectrochemical analysis, 1920–1937," Am. Soc. Test. Mat. Philadelphia (1939).

[2] G. R. Harrison, *Proceedings of the Fifth Conference on Spectroscopy* (John Wiley, New York, 1938), p. 31; M. Slavin, *Proceedings of the Seventh Conference on Spectroscopy* (John Wiley, New York, 1940) p. 51.

[3] R. A. Sawyer and H. B. Vincent, *Proceedings of the Sixth Conference on Spectroscopy* (John Wiley, New York, 1939), p. 54.

[4] H. A. Robinson, Zeits. f. Physik **101**, 658 (1936).

[5] H. Lundergårdh, *Die Quantitative Spektralanalyse der Elemente und ihre Anwendung auf Biologische, Agrikulturchemische und Mineralogische Aufgaben* (G. Fischer, Jena, 1929); *Die Quantitative Spektralanalyse der Elemente. Teil 2. Methodische Verbesserungen und praktische Anleitung für die Ausführing von Analysen in die Gebieten der Biologie, Medizin, Agrikulturchemie und des Bergbaus* (G. Fischer, Jena, 1934).

elements can be made to emit spectra in ordinary flames and the absolute sensitivity is comparatively low for most of them. These are consequences, undoubtedly, of the relatively low temperatures in gas flames.

Higher temperatures characteristic of atmospheric electric arcs between metallic electrodes are necessary and sufficient to produce well-developed first spectra of all elements. Although the thermal mechanism in the arc column is positively established[6] the arc is far from being a homogeneous source. Regardless of the potential applied to the apparatus the voltage drop between arc electrodes rarely exceeds 30 or 40 volts, and most of this drop occurs within the electronic free path near the active cathode spot where electrical excitation produces spectral lines belonging to singly ionized and doubly ionized atoms. Lines caused by impurities are also enhanced in the negative flame.[7] This fact is the basis of the so-called cathode-layer method[8] of spectrochemical analysis. The worst feature of d.c. metal arcs from the standpoint of precision analysis is variability and instability caused probably by wandering of the cathode spot.[3] A practical method of stabilizing metallic arcs is urgently needed. I do not know if magnetic control has been tried.

The favorite light source at the moment is the controlled high voltage condensed spark.[9] This type of source has been studied in some detail[10] and is said to be a high frequency a.c. arc with potential drop of about 50 volts. Here again nearly all of the voltage drop probably occurs at the electrodes since the appearance or enhancement of lines belonging to higher stages of ionization is commonly observed at the poles of condensed sparks. The spectra are always more or less encumbered by air lines and continuous background, which can be suppressed in part by increasing the inductance in the discharge circuit. Relatively large inductance also reduces the intensity of higher stage spectra and decreases the brightness of the source. Whether or not this is to be explained as a reduction in temperature has not been determined. Neither has the fluctuation of temperature with the sinusoidal variation of current in the oscillating discharge of the controlled spark been investigated. But there can be no doubt that, in general, high voltage condensed sparks favor the excitation of second and higher stage spectra at the expense of the spectra of neutral atoms. This may explain the lower absolute sensitivity of trace elements in the spark as compared with the arc. In both cases strong lines of neutral atoms are usually looked for (because the strongest lines of most ionized atoms are in the extreme ultraviolet) and if 90 percent of the atoms are ionized in the spark the effect on the intensity of neutral atom lines is equivalent to a tenfold dilution. If the spectrum lines of neutral atoms are suppressed and the strongest lines of ionized atoms are out of range the practical power of detecting trace elements may be reduced by a large factor.

This brings us to the question: Which line of a spectrum should be consulted to test the presence of the minimum concentration that can be detected spectroscopically? Can the true *raie ultime* be predicted by the theory of atomic and spectral structure?

Twenty-five years ago de Gramont[11] attempted to find a physical basis for his spark *raies ultimes*. He said that: (1) They are not necessarily the strongest or most brilliant spectral lines of the element to which they appertain. (This statement is certainly incorrect.) (2) They resist the introduction of strong self-induction in the condenser discharge circuit. (This is because they are mainly first-spectrum lines.) (3) They are present in arc and flame spectra. (4) When the spectrum of an element furnishes lines spontaneously reversed, the *raies ultimes* will be found among these. (In other words, they involve the normal state, or other low energy state, of the atom.) (5) They belong to "principal" spectral series in all cases where such are known. (Another way of saying they involve the normal state of the atom.)

[6] L. S. Ornstein and H. Brinkman, Physica **1**, 797 (1933–34).

[7] C. Fabry and F. Buisson, J. de phys. **9**, 937 (1910).

[8] L. Strock, *Spectrum analysis with the Carbon Arc Cathode Layer* (Adam Hilger, London, 1936).

[9] O. Fuessner, U. S. Patent 1,971,215, August 21, 1934; R. A. Sawyer and H. B. Vincent, *Proceedings of the Fifth Conference on Spectroscopy* (John Wiley, New York, 1938), p. 1.

[10] H. Kaiser and A. Wallraff, Ann. d. Physik (5) **34**, 297 (1939).

[11] A. de Gramont, Ann. de Chim. (9) **3**, 269 (1915).

In 1924, three years after the discovery of higher multiplicities, the advances which had been made in the interpretation of complex spectra led Meggers, Kiess and Walters[12] to seek some general conclusions as to the relation of the empirical *raies ultimes* to spectral terms. Newly found regularities among spark lines of elements in the first long period seemed to indicate that "the most sensitive spark lines occur without exception, among terms belonging to systems of the largest multiplicity observed in the particular spectrum, and in all cases where the relative term magnitudes are known or temperature classification of the lines exists it is seen that these *raies ultimes* involve the lowest energy level, i.e., the normal state of the ionized atoms." Today it appears that neither of these conclusions is generally valid. At the same time these rules did not appear to apply to arc spectra and a true *raie ultime* which ended on a metastable state was pointed out as an interesting exception to the rule that they always involve the normal state of the atom. Failing to find any positive rules an attempt was made to find some negative ones. "In general, true *raies ultimes* never occur in combinations between terms of the same type ($\Delta l = 0$), nor in intersystem combinations although such transitions may involve the lowest energy level and smaller energy changes." (It seems probable now that neither of these conclusions is universally valid.)

Catalán[13] in 1930 discussed the structure of the first spectra of the first long period of elements, Ca to Zn, and concluded that in every case, except Sc, the *raie ultime* belonged to the transition in which the convergence limit in the second spectrum is the lowest.

In 1934, Meggers and Scribner,[14] on the basis of more recent progress in analysis of spectral structures and correlation with electron configurations, formulated a new rule governing the selection of the *raie ultime* in any spectrum. It is briefly stated as follows: "A *raie ultime* in any spectrum originates with a simple interchange of a single electron between s and p states, usually preferring configurations in which only one electron occurs in such states." A number of cases have since been pointed out where the strongest line characteristic of a spectrum does not involve the normal state of the atom,[15] but nevertheless obeys the above rule.

It seems natural to expect that the *raie ultime* in any spectrum must inevitably be the most intense line of that spectrum. Every experiment in which one element is diluted by another will show that the fainter spectral lines vanish first, while the stronger ones diminish in strength until finally only one, the strongest of all, remains as positive proof of the presence of the element in the lowest concentration that permits its spectrographic detection. The order of lines arranged according to decreasing quantitative sensitivity is the same as the order of decreasing intensity in the spectrum of the pure element.[16] Emission line intensities (barring self-reversal) are directly proportional to the number of radiating atoms in the related states, and if the concentrations at which different lines vanish were susceptible of accurate measurement this would be a quantitative method of observing the relative intensities.

Admitting that the true *raie ultime* of a spectrum is the strongest line of that spectrum, there are three ways of selecting these: (1) by accurately measuring the relative intensities of the stronger lines, (2) by carefully observing the residual or most persistent line for each spectrum as the element is progressively diluted, (3) by asking the quantum theory of atomic spectra.

(1) Methods of measuring the relative intensities of spectral lines by photographic photometry were developed some years ago.[17] For a time they were enthusiastically employed to test the sum rule and theoretical intensities in multiplets and supermultiplets, but at the present moment reliable intensity values remain the outstanding need in spectroscopy. Thus far no spectrum has been completely measured, and

[12] W. F. Meggers, C. C. Kiess and F. M. Walters, Jr. J. Opt. Soc. Am. & Rev. Sci. Inst. **9**, 372 (1924).
[13] A. Catalán, Anal. Soc. Espan. Fis. Quim. **28**, 83 (1930).
[14] W. F. Meggers and B. F. Scribner, J. Research Nat. Bur. Stand. **13**, 657 (1934).
[15] W. F. Meggers and B. F. Scribner, J. Research Nat. Bur. Stand. **14**, 629 (1935); W. F. Meggers and H. N. Russell, J. Research Nat. Bur. Stand. **17**, 126 (1936).
[16] T. Negresco, Comptes rendus **185**, 453 (1927).
[17] L. S. Ornstein, W. J. H. Moll and H. C. Burger, *Objektive Spektralphotometrie* (Vieweg, Braunschweig, 1932); G. R. Harrison, J. Opt. Soc. Am. **24**, 59 (1934).

no precise data exist for comparing the strongest lines from different electron configurations.

(2) Observations of residual or persistent lines that have been published thus far are mainly those of Hartley[18] de Gramont[19] and Löwe,[20] all made with condensed spark discharges and limited to the spectral range 2138–6708A. Several years ago B. F. Scribner and I began a systematic study of residual spectra of 70 elements excited in metallic arc spectra. Various interruptions, especially a tremendous increase in the demands for spectrochemical testing, have delayed its completion. Observations of this kind cannot claim to be infallible because they are made without corrections of any kind and they include the uncertainty of deciding exactly when a spectral line is on the verge of vanishing.

(3) The theory of spectral line intensities was developed 15 years ago,[21] and tables of relative intensities of lines in multiplets[22] and of multiplets in supermultiplets[23] have been published since then. But thus far only intensities of lines belonging to any one configuration of electrons are theoretically known and the theory has not yet been extended to permit comparisons of intensities of lines from two or more configurations. It is of special interest to compare the strongest line from ds^2-dsp with the strongest line from d^2s-d^2p but up to now theory has said nothing on this point. Furthermore, the theoretical intensities now available apply only to cases of pure *ls* or *jj* coupling, whereas there is evidence in many spectra of intermediate coupling, especially for the production of excited states.

Since none of the above methods of selecting strongest lines can at present give a complete answer, I have attempted to get from all of them combined, a tentative list of the strongest lines belonging to neutral atoms of the elements. The data are presented in Table I with atomic number, chemical symbol, ionization potential, low state, its term symbol, excited state, its term symbol, and wave-length of the strongest line in successive columns. Occasional numbers at the extreme right refer to notes at the end of the table.[24]

The ionization potentials (determined from spectroscopic data) are given in volts, and are proportional to the minimum energies required to remove the last bound electron. The values range from 3.89 v for Cs to 24.465 v for He, but only three atoms (K, Rb, Cs) have ionization potentials less than 5 v and only sixteen elements (H, noble gases, halogens, metalloids) have stability exceeding 10 v. The fact that seventy of the chemical elements have ionization potentials less than 10 v, and that these seventy are the identical ones searched for in spectrochemical testing, is probably not an accidental coincidence. It is a consequence of atomic structure and accounts in large part for the success of practical spectrographic analysis when limited to these 70 elements.

Ionization potentials have minimum values when the first electron of a given type appears in an atom, and maximum values when the shell or subshell of this type is complete. Electrons of type p, $(l=1)$, are more firmly bound in general than any others. This fact makes it difficult to excite the spectra of noble gases, halogens, and metalloids in the presence of elements with low ionization potentials, and often places their strongest lines in the extreme ultraviolet avoided in practical analysis. The wave-lengths of the strongest lines characteristic of neutral atoms range from 584A for He to 8521A for Cs, but in practical spectrochemical analysis the range of observation is usually from 2100 to 5000A (ordinary photographic emulsions), or possibly to 6800A (panchromatic emulsions). It will be noticed that the wave-lengths of the strongest lines are inversely proportional (approximately) to the ionization potentials and only 18 (or possibly 20) are shorter than 2000A.

The atomic energy states (1 v = 8106 cm^{-1}) producing the strongest lines are shown in

[18] W. N. Hartley, Phil. Trans. Roy. Soc. **175**, 49, 325 (1884).
[19] A. de Gramont, Comptes rendus **171**, 1106 (1920).
[20] F. Löwe, *Atlas der letzten Linien der wichtigsten Elemente* (T. Steinkopff, Dresden and Leipzig, 1928).
[21] H. N. Russell, Proc. Nat. Acad. Sci. **11**, 314, 322 (1925); A. Sommerfeld and H. Hönl, Sitz. Berlin Akad. Wiss. **9**, 141 (1925).
[22] H. E. White and A. Y. Eliason, Phys. Rev. **44**, 753 (1933); H. N. Russell, Astrophys. J. **83**, 129 (1936).
[23] L. Goldberg, Astrophys. J. **82**, 1 (1935); D. H. Menzel and L. Goldberg, Astrophys. J. **84**, 1 (1936).
[24] Compare with table of "The electron configurations of the 92 elements in their normal atomic states," H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill, New York, 1934), pp. 82–84.

columns 4 to 7. In each case the normal state of the atom is set at 0.0. Although a majority of the strongest lines involve the normal state (that is, when the term is single valued or when polyfold terms are "inverted"), there are a considerable number of instances in which this is not true. Most of these exceptions fall into two classes, (1) those in which the fine structure of the term is "normal" (level with smallest j value has lowest energy as in B, C, Al, Si, Ga, Ge, In, Sm, Gd, Hf, Tl), and (2) those in which the configuration with a single s electron competes successfully with the alternative configuration containing two s electrons (Sc, Ti, V, Fe, Co, Ni, etc.).

Other things being equal, relative intensities of spectral lines are given by the sum rule, that is they are proportional to the statistical weights $(2J+1)$ of the levels involved. Consequently the transitions between the levels with largest L and J values produce the strongest lines. The boron line 2497.73A, for example, is twice as strong as its companion 2496.78A, and the manganese line 4030.76A is twice as strong as the weakest member, 4034.49A, of the well-known triplet.

In any particular spectrum the excitation energies or elevations of atomic states are an important factor in determining the relative intensities of spectral lines. Thus the easily excited first members of the principal series in alkali spectra have on the average 100 times the strength of the second members.[25]

The most important fact displayed in Table I is that in every case the strongest line is produced by a transition between s and p electrons. These correspond, respectively, to orbital moments of 0 and 1 unit, the smallest in atomic systems. In all cases, except those in which p electrons are being added, the ground state is given by a configuration containing either one or two s electrons. Excitation which changes an s electron to a p electron makes possible the reverse transition which results in the emission of one or more spectral lines. Atoms that possess only one valence s electron (alkalis, Cu, Ag, Au, Cr) exhibit the highest absolute sensitivity.

[25] S. A. Korff and G. Breit. Rev. Mod. Phys. **4**, 501 (1932).

Atoms containing two valence s electrons invariably have two configuration possibilities, one containing two s electrons and the other containing one s electron combined with one or more of other types (p, d, f). In such cases it is not always easy to decide which configuration is involved in producing the strongest line. Quantum theory has not been developed to the point where intensities belonging to different configurations can be compared, and no quantitative intensity measurements have been made to answer these questions. The only information available is that from the study of residual spectra or from the structural analyses of spectra for which semiquantitative intensity estimates exist. Data of these kinds indicate that, in general, the configuration with one s electron leads the other with two s electrons in producing the strongest line so long as the excitation energy of the low state in the first case is less than the difference in energy of binding of one and of two s electrons. Thus, the ionization potentials of K (4.32 v) and Ca (6.09 v) show that the second $4s$ electron is bound 1.77 v more firmly than the first. Calcium also has a configuration $3d4s$ but the lowest term it produces is 2.5 v above the ground state. However, in scandium $3d^24s$ yields a term only 1.4 v above the ground state $3d4s^2$ and therefore produces the stronger line. In very complex spectra and in those with wide fine structure, where intermediate coupling of electrons occurs, the observed atomic energy states cannot always be assigned wholly to one configuration, and intensity perturbations may then arise to violate this rule, but up to the present no real exceptions have been found either in arc or in spark spectra. (Apparent exceptions may arise from instrumental causes.)

Atoms with p electrons as valence units always derive their ground states from 1 to 6 of these electrons and are in condition to emit their strongest lines when one of these p electrons is transformed by excitation to the s type. As a class these atoms do not possess high sensitivity and many of them are ignored in spectrochemical analysis as commonly practiced. The carbon-like atoms of this class (C, Si, Ge, Sn, Pb) deserve special comment. Each has low states described by (p^2) ^1S, ^1D, ^3P and the zero level is (p^2) $^3P_0$.

TABLE I. *Strongest lines of the first spectra of chemical elements.*

ATOMIC NUMBER	ELEMENT	I. P. VOLTS	LOW STATE cm^{-1}	(ELECTRONS) LOW TERM	EXCITED STATE cm^{-1}	(ELECTRONS) HIGH TERM	WAVE-LENGTH A
1	H	13.529	0.0	$(s)^2S_{0\frac{1}{2}}$	82,259.8	$(p)^2P_{1\frac{1}{2}}$	1215.66[1]
2	He	24.465	0.0	$(s^2)^1S_0$	171,122.0	$(sp)^1P_1^\circ$	584.33
3	Li	5.37	0.0	$(s)^2S_{0\frac{1}{2}}$	14,903.8	$(p)^2P_{1\frac{1}{2}}$	6707.85
4	Be	9.281	0.0	$(s^2)^1S_0$	42,565.0	$(sp)^1P_1^\circ$	2348.61
5	B	8.28	15.0	$(p)^2P_{1\frac{1}{2}}^\circ$	40,039.0	$(s)^2S_{0\frac{1}{2}}$	2497.73[2]
6	C	11.217	42.3	$(p^2)^3P_2$	60,391.4	$(ps)^3P_2^\circ$	1657.01[3]
7	N	14.48	0.0	$(p^3)^4S_{1\frac{1}{2}}^\circ$	88,109.5	$(p^2s)^4P_{2\frac{1}{2}}$	1134.98
8	O	13.550	0.0	$(p^4)^3P_2$	76,794.0	$(p^3s)^3S_1^\circ$	1302.19
9	F	18.6	0.0	$(p^5)^2P_{1\frac{1}{2}}^\circ$	104,738.0	$(p^4s)^2P_{1\frac{1}{2}}$	954.8
10	Ne	21.47	0.0	$(p^6)^1S_0$	135,889.0	$(p^5s)^1P_1^\circ$	735.89
11	Na	5.12	0.0	$(s)^2S_{0\frac{1}{2}}$	16,973.3	$(p)^2P_{1\frac{1}{2}}^\circ$	5889.95
12	Mg	7.61	0.0	$(s^2)^1S_0$	35,051.4	$(sp)^1P_1^\circ$	2852.13
13	Al	5.96	112.0	$(p)^2P_{1\frac{1}{2}}^\circ$	25,347.6	$(s)^2S_{0\frac{1}{2}}$	3961.53[4]
14	Si	8.12	223.1	$(p^2)^3P_2$	39,954.9	$(ps)^3P_2^\circ$	2516.12[5]
15	P	11.1	0.0	$(p^3)^4S_{1\frac{1}{2}}^\circ$	56,344.0	$(p^2s)^4P_{2\frac{1}{2}}$	1774.94
16	S	10.3	0.0	$(p^4)^3P_2$	55,326.0	$(p^3s)^3S_1^\circ$	1807.31
17	Cl	12.96	0.0	$(p^5)^2P_{1\frac{1}{2}}^\circ$	74,221.4	$(p^4s)^2P_{1\frac{1}{2}}$	1347.2
18	A	15.69	0.0	$(p^6)^1S_0$	95,392.2	$(p^5s)^1P_1^\circ$	1048.22
19	K	4.32	0.0	$(s)^2S_{0\frac{1}{2}}$	13,042.8	$(p)^2P_{1\frac{1}{2}}^\circ$	7664.91
20	Ca	6.09	0.0	$(s^2)^1S_0$	23,652.4	$(sp)^1P_1^\circ$	4226.73
21	Sc	6.7	11,677.3	$(d^2s)^4F_{4\frac{1}{2}}$	29,303.5	$(d^2p)^4G_{5\frac{1}{2}}^\circ$	5671.80[6]
22	Ti	6.81	6843.0	$(d^2s)^5F_5$	26,910.7	$(d^2p)^5G_6^\circ$	4981.73[7]
23	V	6.76	2424.9	$(d^4s)^6D_{4\frac{1}{2}}$	25,253.4	$(d^4p)^6F_{5\frac{1}{2}}^\circ$	4379.24[8]
24	Cr	6.74	0.0	$(d^5s)^7S_3$	23,498.9	$(d^5p)^7P_4^\circ$	4254.35
25	Mn	7.41	0.0	$(d^5s^2)^6S_{2\frac{1}{2}}$	24,802.2	$(d^5sp)^6P_{3\frac{1}{2}}^\circ$	4030.76
26	Fe	7.83	6928.3	$(d^7s)^5F_5$	34,844.0	$(d^7p)^5G_6^\circ$	3581.20[9]
27	Co	8.5	3482.8	$(d^8s)^4F_{4\frac{1}{2}}$	32,430.6	$(d^8p)^4G_{5\frac{1}{2}}^\circ$	3453.50[10]
28	Ni	7.606	204.8	$(d^9s)^3D_3$	29,481.0	$(d^9p)^3F_4^\circ$	3414.76[11]
29	Cu	7.68	0.0	$(s)^2S_{0\frac{1}{2}}$	30,783.7	$(p)^2P_{1\frac{1}{2}}^\circ$	3247.54
30	Zn	9.36	0.0	$(s^2)^1S_0$	46,745.1	$(sp)^1P_1^\circ$	2138.56
31	Ga	5.97	826.0	$(p)^2P_{1\frac{1}{2}}^\circ$	24,788.3	$(s)^2S_{0\frac{1}{2}}$	4172.06[12]
32	Ge	8.09	1409.9	$(p^2)^3P_2$	39,117.7	$(ps)^3P_2^\circ$	2651.18[13]
33	As		0.0	$(p^3)^4S_{1\frac{1}{2}}^\circ$	52,896.9	$(p^2s)^4P_{2\frac{1}{2}}$	1890.5
34	Se	9.5	0.0	$(p^4)^3P_2$	51,001.0	$(p^3s)^3S_1^\circ$	1960.91
35	Br	11.80	0.0	$(p^5)^2P_{1\frac{1}{2}}^\circ$	67,176.9	$(p^4s)^2P_{1\frac{1}{2}}$	1488.4
36	Kr	13.940	0.0	$(p^6)^1S_0$	80,916.0	$(p^5s)^3P_1^\circ$	1235.82[14]
37	Rb	4.159	0.0	$(s)^2S_{0\frac{1}{2}}$	12,816.4	$(p)^2P_{1\frac{1}{2}}^\circ$	7800.23
38	Sr	5.667	0.0	$(s^2)^1S_0$	21,698.5	$(sp)^1P_1^\circ$	4607.33
39	Y	6.5	11,532.1	$(d^2s)^4F_{4\frac{1}{2}}$	29,820.4	$(d^2p)^4G_{5\frac{1}{2}}^\circ$	5466.47[15]
40	Zr	6.92	5888.9	$(d^2s)^5F_5$	27,214.9	$(d^2p)^5G_6^\circ$	4687.80[16]
41	Cb		1050.3	$(d^4s)^6D_{4\frac{1}{2}}$	25,680.4	$(d^4p)^6F_{5\frac{1}{2}}^\circ$	4058.94[17]
42	Mo	7.35	0.0	$(d^5s)^7S_3$	26,320.4	$(d^5p)^7P_4^\circ$	3798.25
43	Ma						
44	Ru		0.0	$(d^7s)^5F_5$	28,571.8	$(d^7p)^5G_6^\circ$	3498.94
45	Rh	7.7	0.0	$(d^8s)^4F_{4\frac{1}{2}}$	29,104.6	$(d^8p)^4G_{5\frac{1}{2}}^\circ$	3434.89
46	Pd	8.3	6564.0	$(d^9s)^3D_3$	35,927.8	$(d^9p)^3F_4$	3404.58[18]
47	Ag	7.54	0.0	$(s)^2S_{0\frac{1}{2}}$	30,472.9	$(p)^2P_{1\frac{1}{2}}^\circ$	3280.68
48	Cd	8.96	0.0	$(s^2)^1S_0$	43,692.2	$(sp)^1P_1^\circ$	2288.02
49	In	5.76	2212.6	$(p)^2P_{1\frac{1}{2}}^\circ$	24,373.1	$(s)^2S_{0\frac{1}{2}}$	4511.32[19]
50	Sn	7.297	3427.7	$(p^2)^3P_2$	34,914.2	$(ps)^3P_1^\circ$	3175.04[20]
51	Sb		0.0	$(p^3)^4S_{1\frac{1}{2}}^\circ$	48,331.9	$(p^2s)^4P_{2\frac{1}{2}}$	2068.38
52	Te		0.0	$(p^4)^3P_2$	46,653.6	$(p^3s)^3S_1^\circ$	2142.75
53	I						
54	Xe	12.078	0.0	$(p^6)^1S_0$	68,046.0	$(p^5s)^3P_1^\circ$	1469.62[21]
55	Cs	3.87	0.0	$(s)^2S_{0\frac{1}{2}}$	11,732.3	$(p)^2P_{1\frac{1}{2}}^\circ$	8521.10
56	Ba	5.19	0.0	$(s^2)^1S_0$	18,060.2	$(sp)^1P_1^\circ$	5535.55
57	La	5.59	4121.6	$(d^2s)^4F_{4\frac{1}{2}}$	20,117.4	$(d^2p)^4G_{5\frac{1}{2}}^\circ$	6249.93[22]
58	Ce						
59	Pr						
60	Nd						
61	—						
62	Sm	5.6?	4020.7	$(f^6s^2)^7F_6$	27,287.6	$(f^6sp)^7G_7^\circ$	4296.75[23]
63	Eu	5.64	0.0	$(f^7s^2)^8S_{3\frac{1}{2}}^\circ$	21,761.3	$(f^7sp)^8P_{4\frac{1}{2}}$	4594.02[24]
64	Gd		1719.1	$(f^7ds^2)^9D_6^\circ$	25,376.4	$(f^7dsp)^9F_7$	4225.85[25]
65	Tb						
66	Dy						
67	Ho						
68	Er						
69	Tm						

TABLE I.—*Continued.*

ATOMIC NUMBER	ELEMENT	I. P. VOLTS	LOW STATE cm^{-1}	(ELECTRONS) LOW TERM	EXCITED STATE cm^{-1}	(ELECTRONS) HIGH TERM	WAVE-LENGTH A
70	Yb	6.2	0.0	$(s^2)^1S_0$	25,068.2	$(sp)^1P_1^\circ$	3987.99[26]
71	Lu	5	1993.9	$(ds^2)^2D_{2\frac{1}{2}}$		$(dsp)^2F_{3\frac{1}{2}}^\circ$	[27]
72	Hf		4567.6	$(d^2s^2)^3F_4$		$(d^2sp)^2G_5^\circ$	[28]
73	Ta		5621.0	$(d^3s^2)^4F_{4\frac{1}{2}}$		$(d^3sp)^4G_{5\frac{1}{2}}^\circ$	[29]
74	W		2951.3	$(d^5s)^7S_3$		$(d^5p)^7P_4^\circ$	[30]
75	Re	7.85	0.0	$(d^5s^2)^6S_{2\frac{1}{2}}$	28,889.6	$(d^5sp)^6P_{3\frac{1}{2}}^\circ$	3460.47[31]
76	Os	8.7	0.0	$(d^6s^2)^5D_4$	34,365.3	$(d^6sp)^5F_5$	2909.06[32]
77	Ir	9.2	2835.0	$(d^8s)^4F_{4\frac{1}{2}}$	42,131.8	$(d^8p)^4G_{5\frac{1}{2}}^\circ$	2543.97[33]
78	Pt	8.9	0.0	$(d^9s)^3D_3$	37,590.7	$(d^9p)^3F_4^\circ$	2659.44
79	Au	9.2	0.0	$(s)^2S_{0\frac{1}{2}}$	41,174.2	$(p)^2P_{1\frac{1}{2}}^\circ$	2427.95
80	Hg	10.38	0.0	$(s^2)^1S_0$	54,065.7	$(sp)^1P_1^\circ$	1849.68[34]
81	Tl	6.07	7792.7	$(p)^2P_{1\frac{1}{2}}^\circ$	26,477.5	$(s)^2S_{0\frac{1}{2}}$	5350.46[35]
82	Pb	7.38	10,648.0	$(p^2)^3P_2$	35,285.0	$(ps)^3P_1^\circ$	4057.82[36]
83	Bi		0.0	$(p^3)^4S_{1\frac{1}{2}}^\circ$	32,588.0	$(p^2s)^4P_{0\frac{1}{2}}$	3067.72[37]
84	Po						
85	—						
86	Rn	10.689	0.0	$(p^6)^1S_0$	55,989.0	$(p^5s)^3P_1^\circ$	1786.07[38]
87	—						
88	Ra	5.176	0.0	$(s^2)^1S_0$	20,715.7	$(sp)^1P_1^\circ$	4825.91[39]
89	Ac						
90	Th						
91	Pa						
92	U						

[1] Data in Table I are taken from *Atomic Energy States* by Bacher and Goudsmit (McGraw-Hill, New York, 1932) except where otherwise indicated by notes. Wave-lengths greater than 2000A are taken from *M.I.T. Wavelength Tables* (John Wiley, New York, 1939); shorter than 2000A from *Tabelle der Hauptlinien der Linienspektren aller Elemente* (Kayser-Ritschl, Julius Springer, Berlin, 1939).

[2] 0.0 = $(p)^2P_{0\frac{1}{2}}$.

[3] 0.0 = $(p^2)^3P_0$.

[4] 0.0 = $(p)^2P_{0\frac{1}{2}}$.

[5] 0.0 = $(p^2)^3P_0$.

[6] 0.0 = $(ds^2)^2D_{1\frac{1}{2}}$.

[7] 0.0 = $(d^2s^2)^3F_2$.

[8] 0.0 = $(d^3s^2)^4F_{1\frac{1}{2}}$

[9] 0.0 = $(d^4s^2)^5D_4$.

[10] 0.0 = $(d^7s^2)^4F_{4\frac{1}{2}}$.

[11] 0.0 = $(d^5s^2)^2F_4$.

[12] 0.0 = $(p)^2P_{0\frac{1}{2}}$.

[13] 0.0 = $(p^2)^3P_0$.

[14] Intersystem combination?

[15] 0.0 = $(ds^2)^2D_{1\frac{1}{2}}$.

[16] 0.0 = $(d^2s^2)^2F_2$.

[17] 0.0 = $(s)^6D_{0\frac{1}{2}}$.

[18] 0.0 = $(d^{10})^1S_0$.

[19] 0.0 = $(p)^2P_{0\frac{1}{2}}$.

[20] 0.0 = $(p^2)^3P_0$, cf. W. F. Meggers, J. Research Nat. Bur. Stand. **24**, 153 (1940). In a tin arc 3175A may appear weaker than 3262A because of more self-reversal in the former.

[21] Intersystem combination?

[22] 0.0 = $(ds^2)^2D_{1\frac{1}{2}}$.

[23] 0.0 = $(f^{6}s^2)^7F_0$. W. Albertson, Phys. Rev. **47**, 370 (1935); **52**, 644 (1937).

[24] H. N. Russell and A. S. King, Astrophys. J. **90**, 155 (1939).

[25] 0.0 = $(f^7ds^2)^9D^9$. W. Albertson, Phys. Rev. **47**, 370 (1935).

[26] W. F. Meggers and B. F. Scribner, J. Research Nat. Bur. Stand. **19**, 651 (1937).

[27] W. F. Meggers, unpublished.

[28] 0.0 = $(d^2s^2)^3F_2$.

[29] 0.0 = $(d^3s^2)^4F_{1\frac{1}{2}}$, C. C. Kiess and H. K. Kiess, Bur. Stand. J. Research **11**, 277 (1933).

[30] 0.0 = $(d^4s^2)^5D_0$.

[31] W. F. Meggers, Bur. Stand. J. Research **6**, 1027 (1931).

[32] W. Albertson, Phys. Rev. **45**, 340 (1934).

[33] W. Albertson, Phys. Rev. **54**, 183 (1938).

[34] A. T. Williams (Nature **124**, 985 (1929)) maintains that 1849A is a theoretical *raie ultime* but not an experimental one, and that the true *raies ultimes* of Hg are, in all conditions, 2537 and 1942A. Theory and experiment (G. S. King and J. H. Van Vleck, Phys. Rev. **55**, 464 (1939)) agree that the strengths of 1849 and 2537 of Hg are in the ratio 50 to 1.

[35] 0.0 = $(p)^2P_{0\frac{1}{2}}$.

[36] 0.0 = $(p)^2P_0$.

[37] The excitation potential of $(p^2s)^4P_{2\frac{1}{2}}$ is 2.0 v higher than $(p^2s)^4P_{0\frac{1}{2}}$.

[38] Intersystem combination? E. Rasmussen. Zeits. f. Physik **62**, 494 (1930); **80**, 726 (1933).

[39] E. Rasmussen, Zeits. f. Physik **87**, 607 (1934).

One might expect $(p^2)\,{}^3P_2-(ps)\,{}^3P_2^\circ$ to be the strongest line and this appears to be true except for Sn and Pb in which cases large departures from *ls* coupling in excited states probably entail intensity perturbations. However, even here as everywhere else the *configuration change* producing the strongest lines is $s \leftrightarrow p$.

Atoms whose spectra contain more than one multiplicity of terms have intersystem combinations as resonance lines. Although these inter-

system transitions require the least energy of excitation they are never the strongest lines (except possibly in the heavy noble gases where the excitation difference $^3P_1 - {}^1P_1$ increases rapidly).

Summarizing this discussion: Among conventional light sources electric arcs are best qualified to excite the first spectra of the elements. The strongest lines invariably result from a transition between s and p electrons in the atoms. If the configuration for the normal state contains a single s electron the atoms have extraordinary spectral sensitivity. If the configuration for the normal state contains two s electrons, the strongest line may involve a metastable state belonging to an alternative configuration with one s electron, provided that the excitation of this metastable state is less than the difference in binding of one and of two s electrons. Valence electrons of p type are in general more firmly bound so that noble gases, halogens and metalloids have relatively low spectral sensitivity. Differences in absolute sensitivity appear to be related to atomic structure mainly on account of differences in binding forces on s and p electrons. The notable success of practical spectrographic analysis for seventy elements is related to the fact that these elements have ionization potentials less than 10 v, and strongest lines greater than 2000A in wave-length.

Specifications and Testing of Spectrochemical Apparatus*

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THE purpose of this paper is to discuss, on the basis of several years of experience in the design and testing of apparatus for industrial spectrochemical analysis, what characteristics should be expected in such equipment; how to test the equipment for shortcomings or defects; and how to apportion the accidental errors of the analytical process among the different steps of the process. The treatment will be limited chiefly to equipment for emission spectrography, although some of the equipment is also applicable to absorption work.

The light source will be considered first since it is, chronologically at least, the first piece of equipment encountered in analysis. As the authors have previously stated, the choice of a suitable light source is the major part of any development problem in spectrochemical analysis, and the errors arising from the fluctuations of the light source are likely to be the largest errors in the final result. Characteristics of light sources have been discussed at previous conferences both by the present authors and by others, and time does not permit detailed re-examination of the topic. However, although until recently little but simple arcs and sparks were offered in the way of light sources by manufacturers, an increasing number of more elaborate sources, such as controlled sparks and high voltage arcs, have lately appeared on the market. We may accordingly inquire what may be asked of such sources in general.

A source for industrial use should be sturdy enough for continuous operation, 24 hours a day and 7 days a week, without overheating, without deteriorating and without significantly altering its emission characteristics; it should operate from the industrial mains and be provided, if necessary, with automatic controls to compensate possible fluctuations in supply voltage and frequency; it should be intense enough to provide an adequate exposure, without a condensing lens, in not over two minutes, with the source 10 inches or more from the slit. The reproducibility of results from the source should be determined with carefully prepared samples; the standard deviation should certainly fall within the maker's claims and compare favorably with results obtained by other workers with similar samples and sources. The procedure for differentiating the source error from the other errors in spectrochemical determinations will be considered after the other instruments and sources of error have been discussed.

As with the light source, so with the spectrograph, there is no universal instrument. The choice between a prism or a grating instrument, and the choice of type and style of mounting can be left, to a considerable degree, to taste and circumstance. The spectrograph should, however, have dispersion enough, for the spectra to be studied, to permit a slit-width of at least 25μ, and preferably of 50μ, without undue interference of neighboring lines with each other; the optics should be sealed from the dust of industrial laboratories, or they should be able to withstand cleaning at reasonable intervals, without harm; the mounting should be rigid enough to withstand the vibration of industrial buildings over long periods without readjustment.

Every spectrograph should be tested for light leakage, for stray and scattered light, and for definition. It is well to write specifications on these points in the purchase order, and every spectrographer should satisfy himself that the requirements have been met.

Leakage of light occurs through the housing and plateholder. It seems almost too obvious to mention that the instrument should be light-tight and yet manufacturers sometimes seem to intend their instruments for use only in dark rooms. It is, however, neither necessary nor desirable that the spectrograph room should always be dark. It is often preferable to have the source in the spectrograph room, and to carry on sample preparation while exposures are being made. Anyone may make a test for light leaks simply by looking into the plateholder opening of the spec-

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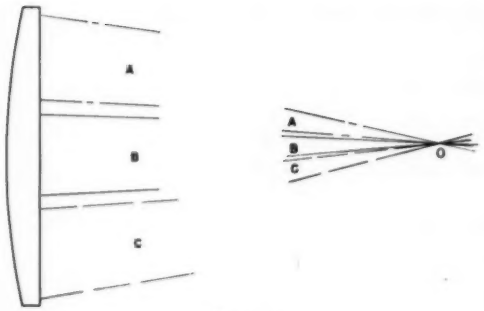

FIG. 1.

trograph, with his head covered with an opaque cloth, while an assistant carries a 500-watt electric bulb about the spectrograph. Any significant leak should be revealed.

As a check for leaks in the plateholder and dark slides, a fast plate may be placed in the plateholder, the dark slide drawn, and a 500-watt bulb moved about the plateholder end, and, if desired, about the whole spectrograph. If there are no leaks, the plate on development will be fog-free.

Of the light which enters the spectrograph slit, a certain amount is reflected or scattered out of the normal beam by the surfaces of the optics, the mountings, and spectrograph walls. In this respect, autocollimating instruments usually give somewhat more trouble than those with separate collimator and camera lenses. It is the problem of the instrument maker to see that only a negligible amount of such scattered light reaches the photographic emulsion to cause fog and false background; and this end can usually be achieved by careful design of lens curvatures, by slight tilt or rotation of the lens and by the use of baffles and diaphragms. While a preliminary test for stray light may be made visually by observation, at the plateholder slot, of an intense line spectrum, when no light should be seen except that coming from the optics to the line images, the final test should be made photographically and under conditions much more severe than those likely to be met in practice. Accordingly, with the slit wide open, a five- or ten-minute exposure should be made on a rapid plate with a 5-ampere iron arc condensed on the slit; or any similar exposure may be employed which, for the spectrograph used, is perhaps one hundred times that needed for a good spectrogram. If the plate, after processing, shows no signs of fogging by stray light, it is reasonably certain that trouble from this source will not arise.

As important as the elimination of stray light is the need for good definition in the spectra. It is true that extreme resolving power is ordinarily not demanded in spectrochemical work and that the slit-widths used are, in general, rather wide. It is, however, essential to accuracy that, with these wide slits, uniform flat-topped lines be produced. The precision of the results will be affected by optical aberrations, which result in hollow lines or in irregularly shaped lines with fuzzy edges or with false companions, caused either by prism and lens aberrations or, in the case of gratings, by ghosts. Experience has shown that every user of a spectrograph should assure himself by tests that its quality is adequate. Test plates submitted by the manufacturer should not be relied upon unless they have been taken under carefully specified conditions. They may otherwise have been taken with weak exposures and with high contrast plates—a condition which, because the faint imperfections may have intensities below the high plate inertia, suppresses the effects of stray light, of faint line components and of poor line definition. High contrast plates are useful for practical work but should not be used for tests of quality.

The first and simplest test of spectrograph quality is to make a focus plate using an emulsion of moderate speed and contrast, such as an Eastman II–0, and a light source emitting fine lines. The spectrograms at the best focus, when examined with an eyepiece, should show very sharp line images without any fuzziness or faint companion lines on either side. It is well to use a spectrum with a wide range of intensity, since under various conditions of imperfection, defects may appear differently at different densities.

With some experience it is possible to judge whether or not the line sharpness is adequate. If it is not, additional tests are required to locate the seat of the trouble. In any case, such tests may be desirable, if too much confidence is not to be placed in subjective judgments of line appearance.

A simple but searching test described by Hart-

mann[1] is readily carried out and does not require great experience in interpretation. It rests on the fact, Fig. 1, that all rays of one wave-length passing through the slit and optical system should be brought to a focus in the same sharp line image, but imperfections or aberrations in the optics may cause the beams traversing different segments of the system to come to a focus not only at different lens-plate distances, but also at different plate positions. If every part of the optics contributes to each part of the line image, a fuzzy or irregular line will result; or if different beams form different parts of the line, a crooked line will result. The test is made in the second manner so that the line images formed by different parts of the optics can be compared in position and sharpness. The slit is opened to a width of about $10\,f\lambda/d$ so that the central maximum of the diffraction pattern of the slit is much narrower than the collimator lens. A small light source placed before the slit on the collimator axis sends light through a narrow central region of the optics, while if the source is displaced to either side, regions or strips of the optics to either side of the center are progressively illuminated. At the University of Michigan an uncondensed spark between iron or copper electrodes, one-eighth inch in diameter, with a one-eighth-inch gap, has been found satisfactory as a light source. A lens before the slit to image this source on the optics shortens the exposure considerably.

With the aid of a Hartmann diaphragm a series of adjacent spectra are recorded on a plate as the light source is moved across the field, so that successive sections of the optics are illuminated. It is desirable to include at least five positions. The spectra should be made at the setting of best focus. However, especially if the optics are imperfect, it may be difficult to determine the setting exactly, and in that case, two or three sets of test spectra can be made at settings near to the apparent best focus. It is clear that in the ideal case, the five beams from the five regions should come to a focus at the same plate setting, giving, for each wave-length, five spectra in perfect alignment (Fig. 2(A)). A progressive displacement will be found before (Fig. 2(B)) or behind (Fig. 2(C)) the best focus.

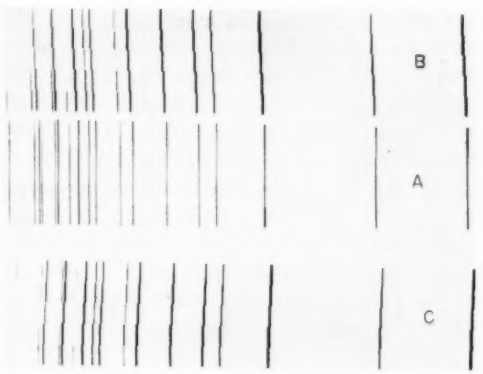

FIG. 2.

If, however, there are significant aberrations or inhomogeneities in the prism or lens material, some of the beams will be diverted from their proper direction. There will be no plate position at which all five spectral lines fall in line, nor will the out-of-focus spectra show the progressive displacements of 2(A) or 2(B). Rather, at different settings, two or more spectra will line up, while the others will be more or less displaced. Such results as Fig. 3(A), (B), or (C) will be obtained. Since, when the whole optics is illuminated at once, the spectral line receives contributions from all the sections, it will have a total width corresponding to the spread of the different line positions. Accordingly, the amount of the dis-

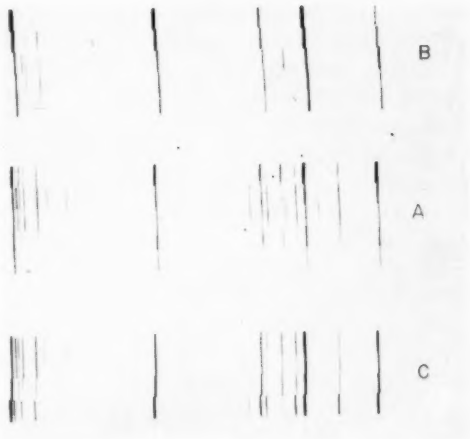

FIG. 3.

[1] J. Hartmann, Zeits. f. Instrumentenk. **20**, 47 (1900).

placement can be measured with a comparator, and if a tolerance is placed on permissible line width, a decision can be reached as to what sections of the optics must be covered in order to attain this width.

When the Hartmann test reveals defects in the optics the question arises as to which component of the system is responsible. Although the lenses, or, in the Littrow type, the totally reflecting prism, may be responsible, suspicion falls first on the dispersing prism or prisms. The difficulty of obtaining sufficiently large homogeneous pieces of glass, and especially of quartz, leads sometimes to the use of second-quality material. If another prism is available, it can be substituted and the test repeated to see whether the result is altered. If substitution is impossible, or if suspicion falls on the lens system, a test can be made without the prism. In the Littrow type a front-surface plane mirror of optical quality can be placed behind the lens, and the slit image photographed as before. For the Babinet-Bunsen type of instrument, if the angle of deviation cannot be reduced to zero, it may be necessary to remove the lenses and slit and set them up for the test on an optical bench or a table. Modifications for particular cases will, in general, be easily devised.

While the Hartmann test is simple in interpretation and extremely searching, it has the limitation that it examines whole regions of the optics at a time rather than each point. A detailed examination may be made by the "knife-edge" test of Foucault.[2] In this test the image of a pinhole or of a narrow slit is observed, either with the unaided eye placed close to the image or with a low power telescope focused on the lens. The lens should be seen filled with light, since each point of the lens contributes to each point of the image. A knife edge passed through the focal plane should cut all beams simultaneously and the whole lens should become dark suddenly and uniformly. Any remaining bright areas indicate imperfections or aberrations which cause the beam to be diverted from the true image. The interpretation of the knife-edge test requires some experience, which can be gained by the examination of lenses the condition of which is known.[3]

In the case of instruments manufactured under modern interferometric control, it is to be expected that tests such as those described above will show that the whole aperture of the optics is usable. Certainly no new instrument should be accepted if appreciable defects are disclosed. Older instruments may require the covering of defective areas of the optics by screens before sharp lines can be obtained. It should be remembered that such diaphragming will reduce the illumination. While the resolving power should be improved over that of the original condition, it will be less than the ideal resolving power if the net thickness of the prism is reduced—that is, if one edge of the prism is covered. If the illumination and resolving power losses are significant, it may be advisable to replace the defective parts.

The choice of photographic emulsion and of processing technique does not, perhaps, strictly come within the scope of this paper. A few comments may, nevertheless, not be amiss. The emulsion should be of as high contrast and as fine grain as is consistent with the range and magnitude of the spectral intensities to be handled. High contrast increases the sensitivity to small changes in concentration, while fine grain reduces the accidental errors in photometric measurement. Slowness of the emulsion, which commonly accompanies these characteristics, is not necessarily a handicap, since it is usually desirable to make the exposures long enough to consume a reasonable amount of the sample.

Development should be carried out in as uniform and reproducible a manner as possible, with enough agitation to avoid Eberhard effect and to give rapid, uniform results. Some form of mechanical rocking or agitation is probably the easiest and simplest procedure. Drying over a hot plate in an air blast results in a great time-saving.[4]

The microphotometer is the last piece of equipment to be discussed. Choice of a suitable microphotometer presents, perhaps the greatest prob-

[2] *Recueil des travaux de Léon Foucault* (Paris, 1878), p. 232.

[3] A description of the procedure with illustrative examples is found in J. Strong *Procedures in Experimental Physics* (Prentice-Hall, New York, 1938), p. 69.

[4] H. B. Vincent and R. A. Sawyer, Spectrochimica Acta 1, 131 (1939).

lem to the spectrographer who must attain speed and accuracy. It is desirable, then, to discuss briefly the characteristics which seem to be desirable for nonrecording or spotting microphotometers, the type in general use for line spectrochemistry, and the type to which these remarks are confined.

Since many of the present-day prism spectrographs of medium and large size have standardized on 4×10-inch plates, a microphotometer should have a plate carriage capable of covering the full area of such a plate without resetting. It is desirable, also, that means be provided for inserting larger plates without cutting. Slides or other means of rapid motion should permit ready translation from point to point in any spectrum or from one spectrum to another, while a screw motion for final adjustment should be provided, together with an auxiliary slow motion to permit traversing a selected line slowly enough to ensure a full reading of the indicating instrument, without excessive care. It should be possible to view a considerable length of the spectrum, at least $\frac{1}{2}$ inch, at one time, preferably in an enlargement on a screen, so as to identify any desired line and bring it into position without delay. A further help for rapid identification is the projection beside the unknown spectrum of a marked reference spectrum. The plate carriage should provide for easy and rapid mounting and alignment of the plate. The plate, the indicating scale, and the screen for viewing the spectrum should be located so as to permit their easy observation in rapid succession, without tiring movements of the eyes or head.

It should be possible to change the area measured on the plate readily and reproducibly, both in length and width. The area which can be used depends on the line width and curvature and on the resolution required. It should be as large as possible, however, not only to increase the luminous energy available, but also to decrease the error due to plate grain. A range of from 5 to 50 microns, in width, and from 0.5 to 5.0 mm in length, should be adequate.

The indicating system should be rapid and extremely stable. The galvanometer period should not be over 2 seconds. The light-sensitive element should be quick in response, free from thermal effects, and not subject to fatigue or to sensitivity changes caused by fluctuations in temperature or to after effects of illumination. The light source should be free from unsteadiness or changes in intensity to at least $\frac{1}{10}$ of 1 percent. The scale readings, with the minimum photometering area, for the full-opaque to clear-plate change should be at least 250 scale divisions.

It should be possible to install and adjust a plate or film in the microphotometer ready for reading in 10 seconds or less, and to read at least five preselected, nonconsecutive lines in one minute. The convenience and ease of operation should be such that an operator can maintain this speed of working all day without undue strain or fatigue.

Aside from fluctuations in the light-source intensity and from fatigue effects and sensitivity changes in the light-sensitive system, a chief cause of error in microphotometer practice is stray or scattered light which enters the detecting system irregularly. The amount of the light, and hence of the error, is not constant, since it depends on the density of the emulsion in the neighborhood of the area photometered. This error was first observed by Schwarzschild and Villiger[5] and has recently been investigated by Keck.[6]

Keck determined the amount of the error caused by stray light by replacing the photographic plate with a movable, sharp, single-slit jaw. Beginning at the optic axis this jaw was moved by a measured amount, x, to cut off more and more of the field, and the amount of light reaching the cell was observed. For x larger than half the width of the projected image of the slit on the focal plane, only scattered light enters the cell. Typical data taken by Keck on a Zeiss recording microphotometer are shown in Fig. 4 which gives the stray light reading in percent of the normal line reading. Curve 1 is for a jaw with upper surface blackened, 2 with upper surface polished, and 3 with blackened jaw covered with a cover glass. Since the effect is 1 percent or less of the normal reading, a more sensitive recording device is required than the normal one. The large difference between curves 1 and 2,

[5] K. Schwarzschild and W. Villiger, Astrophys J. **23**, 287 (1906).

[6] P. H. Keck, Zeiss Nachrichten **10**, 24 (1936), reprinted as Zeiss Bulletin, Mess. 765.

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with blackened and polished top, respectively, for the slit jaw, shows that a large part of the effect is caused by light reflected back from the objective.

The errors which arise in spectrochemical analysis are of two kinds: systematic, and accidental or random. The systematic errors arise from such causes as incorrectly analyzed standard samples for calibration, faulty methods or standards in the calibration patterns, plate background caused by stray light in the spectrograph or by chemical fog, emulsion faults, stray light in the microphotometer, zero drift or sensitivity changes in the measuring system. Methods of testing for and evaluating many of these errors have been discussed. Every effort should be made to determine and eliminate these errors or to evaluate them and correct for their effects.

Accidental or random errors have many causes, such as light-source fluctuations, inhomogeneity in the samples, variations in emulsion thickness and sensitivity and in processing, plate grain, fluctuations in microphotometer light source, vibrations of the galvanometer, etc. They cannot be wholly eliminated, but careful design and choice of instruments and techniques can reduce them. If the sources of random error are numerous enough, the random errors follow a Gaussian distribution. If a considerable number of observations are taken, the standard deviation may be computed as $\sigma=[\Sigma d^2/(n-1)]^{\frac{1}{2}}$ where Σd^2 is the sum of the squares of the deviations from the mean of the individual results, and n, the number of observations. In a Gauss distribution, 67 percent of the results should deviate from the mean by not more than the standard deviation.

In spectrochemical analysis the accidental errors may be classified in four major groups: (1) errors in microphotometer measurements, (2) photographic emulsion errors, (3) light source errors and (4) errors from sample inhomogeneity. If the standard deviations resulting from these four causes are called σ_1, σ_2, σ_3 and σ_4, respectively, the total standard deviation will be given by $\sigma=(\sigma_1^2+\sigma_2^2+\sigma_3^2+\sigma_4^2)^{\frac{1}{2}}$. As pointed out by Kaiser[7] these four σ's may be separated and determined.

Kaiser used as an example a set of measurements for the determination of antimony in lead, and his results will be given to illustrate the method. Repeated measurements on the same spectral line, of density about 1.0, determined the standard deviation in terms of percentage of the galvanometer deflection σ_1, caused by microphotometer reading. By the use of the emulsion calibration curve and the analytical curve, this error was converted into the error in the determination of Sb in the sample and found to be 0.2 percent.

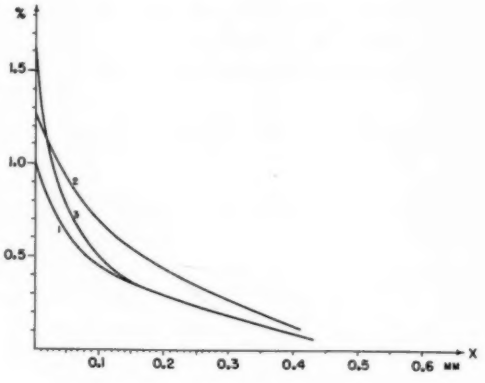

FIG. 4.

Next, measurements were made of the relative intensities of two mercury lines of neighboring wave-lengths, in a series of exposures on the same plate. The source was assumed to be constant. The error in the results is, then, the sum of σ_1 and σ_2, or $\sigma=(\sigma_1^2+\sigma_2^2)^{\frac{1}{2}}$. Since σ_1 is known, σ_2 may be calculated. Using the percentage error in the Sb determination which would have resulted from the same σ in measurements on lines of similar density, it was found that with lines 1.5 mm apart on the plate, with a photometered area 0.1 mm by 1 mm, and with process plates, $\sigma=0.85$ percent and thus $\sigma_2=0.83$ percent. With lines 12 mm apart $\sigma_2=1.4$ percent, showing that plate irregularities increase with distance on the plate. Tests with smaller photometered areas showed that for nearby lines the error in measuring relative intensities is nearly proportional to $1/\text{area}^{\frac{1}{2}}$.

Next a series of measurements on samples, all cut from the same piece of Sb–Pb alloy and assumed to be perfectly homogeneous ($\sigma_4=0$), gave a standard deviation, calculated from

[7] H. Kaiser, Zeits. f. tech. Physik **17**, 227 (1936).

$\sigma=(\sigma_1^2+\sigma_2^2+\sigma_3^2)^{\frac{1}{2}}$, of 1.12 percent. Using the previous values, $\sigma_1=0.2$ percent, $\sigma_2=0.83$ percent, it is found that the error caused by source irregularities, σ_3, is 0.73 percent.

Finally, then, for the whole series of analyses in the test set, the mean error, calculated from $\sigma=(\sigma_1^2+\sigma_2^2+\sigma_3^2+\sigma_4^2)^{\frac{1}{2}}$, is 1.7 percent, whence by substitution of the previous values for σ_1, σ_2, σ_3 it follows that the sample error, σ_4, is 1.28 percent.

It should be said that the figures given above represent an unusually favorable case. The method outlined can, however, be applied in any case to evaluate the different errors. Obviously, since they enter in all the steps, the photometer and plate errors must be smaller or of the same magnitude as the source and sample errors, or they will conceal the other variations.

Such a determination of the magnitude of the various accidental errors is essential to the intelligent analysis of spectrochemical results. It is recommended to all spectrographers and spectrochemists, and especially to those who have preconceived notions as to the accuracy of their results.

Spectrochemistry has developed to the point where equipment and methods should face the acid test of the precision attainable by their use. The accuracy found in the example just given cannot be attained with all sorts of samples or for all ranges of concentration. However, all equipment and every analysis technique should be tested to make sure that the precision is as high as claimed by the makers of the equipment, or by the authors of the technique, and as high as that attained in similar problems with other equipment and techniques.

A New Projection Comparator-Densitometer*

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The 1940 Applied Research Laboratories' projection comparator-densitometer, using spectrum plates either 2″×10″ or 4″×10″, provides dual projection of a sample spectrogram and a master onto a translucent screen mounted directly before the operator. Using a slit system that moves into contact with the plate; a vacuum photo-cell, a two-stage compensated amplifier, and sturdy ammeter, the comparator-densitometer provides transmission readings on any spectral line, accurate to a few tenths of a percent. The unit is fast in operation allowing the operator to read easily as many as six lines per minute. Operating from 115-v, 60-cycle power supply, it achieves this accuracy with the minimum amount of care and upkeep.

INTRODUCTION

ANYONE who has witnessed the projection of a spectrogram taken on an instrument of high resolution appreciates the fact that this method of presentation is unique in its ability to demonstrate interesting detail. Anyone who has used a projection system in routine work either for qualitative or quantitative analysis can appreciate how much less eye strain is caused by it, compared to systems employing eyepieces and microscopic objectives.

It is because of these inherent advantages of projection systems that they are being used very generally today. Three typical systems are illustrated in Fig. 1. Each of these systems prevents the operator from examining projected detail carefully, as to get close to the screen he must of necessity interfere with projection. An alternative system is used in the new Applied Research Laboratories' plate projector which does not have this disadvantage. It employs a translucent screen positioned so as to be immediately in front of the operator. The system is illustrated in Fig. 2. Two plates are projected, one above the other, directly before the operator. He can examine the projected image at his normal reading distance or can scrutinize it at close range when necessary.

PROJECTION

Referring to Fig. 1 again, it will be seen that the third system represents a dual projection which allows direct visual comparison between a sample spectrogram and a master plate. This system was introduced in 1936 on the A.R.L. Projection Comparator. The master plate furnished provided an iron spectrum for alignment, positions and symbols of spectral lines, of seventy elements and a linear wave-length scale allowing the measurement of the wave-length of any line to 0.1A. The last feature was possible only because of the uniformity of dispersion of the A.R.L. grating spectrograph. This projector was shown at the 1937 conference and evoked so much interest among owners of other types of spectrographs that a modified form was produced, suitable for two-inch glass plates instead of the 35-mm film for which it was originally designed. Master plates were improvised by marking certain lines on a comparison spectrum photographed on a two-inch plate.

The present plate projector represents an outgrowth of the previously mentioned ones. However, it is an entirely new instrument in its many mechanical and optical features, designed entirely for the use of plates rather than films. The optical system is illuminated by a 250-w lamp source, which is completely enclosed in a housing through which air is drawn by means of an adequate motor driven blower.

The illuminating system is shown in Fig. 2. Two condensing lenses at opposite sides of the housing pass the light onto 45° metal mirrors. The light is thus reflected up through the spectrum plates and into the projection lenses. With the mirrors in the projection system shown in Fig. 2 an optical path 34 in. long is obtained which gives a magnification of 21× on the screen. The two projections have clean cut edges

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940.

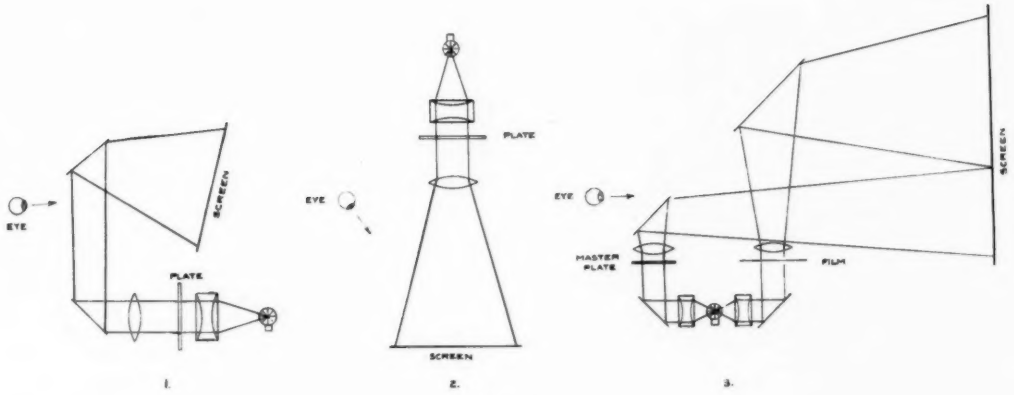

FIG. 1.

which can be adjusted so that the lower master projection is directly below the sample projection with no space between. This allows for accurate comparison of spectral line positions on the two plates. Front surface mirrors also make for sharp images of the lines. The plates are held in convenient holders arranged so that a number of spring strips hold the plates against machined flats. The plates are merely slipped into place, no clips or adjustments being necessary. For the master, a holder for a $2'' \times 10''$ plate is supplied. A carefully machined slot aperture allows a width of $\frac{5}{32}''$ to be projected all along the plate. This in combination with a cross motion of the plateholder allows several master spectrograms to be photographed on the two-inch plate and be projected in turn as they are moved over the aperture.

SPECTRAL LINE IDENTIFICATION

A front view of the comparator-densitometer is shown in Fig. 3. The spectrograms to be analyzed may be photographed on either $2'' \times 10''$ or $4'' \times 10''$ plates. Changing from the large to the small size merely involves placing two plateholder members in position and fastening them with thumb screws. Plateholders are held in a frame, a gear and rack furnishing a cross feed on the spectrum plate to be analyzed. Motion along the plate is achieved by mounting the frame on four ball bearing rollers which move on stainless steel ways, one flat, the other round. A large knob at the front of the projector controls this motion through the use of a continuous steel tape. A vernier motion is obtained with a second knob by means of an eccentric cam and a clutch on the main knob. Besides these motions the frame can be moved across by hand, without movement or damage of the main drive knob system. All control knobs are mounted on the front of the comparator-densitometer unit to permit easy and fast operation.

Having an excellent method of projecting spectrograms and identifying the various lines to be used in an analysis, the next problem is to measure the transmission values of these lines so that exact quantitative analyses can be performed. In 1937 Applied Research Laboratories announced their first photoelectric densitometer.

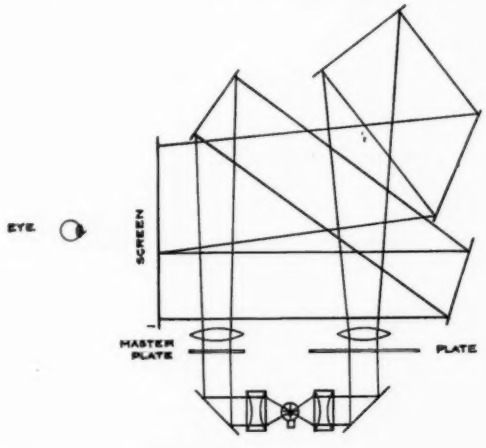

FIG. 2.

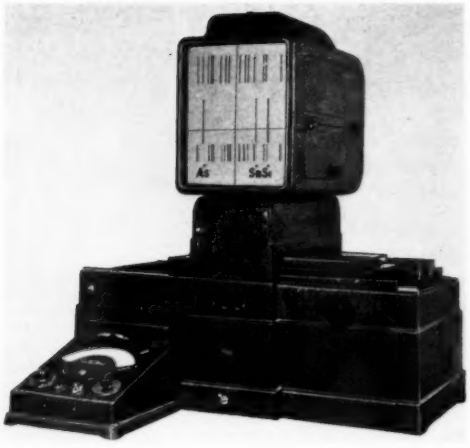

FIG. 3.

It employed a system of projection onto a screen, and utilized a fine slit in the screen behind which was mounted the photo-cell and single-stage amplifier. The output of this amplifier was used to actuate a quick reading microammeter. To achieve stability the amplifier was battery operated while to compensate for line fluctuations, a bridge circuit varied the photo-cell voltage and hence its sensitivity in an opposing manner to the change in lamp brightness. With this system a ten-percent change in line voltage caused only a small fraction of a percent change in meter readings. To obtain a transmission reading of a line, it was moved over the slit on the screen with a vernier screw control manually operated. Careful manipulation gave accurate and reproducible readings.

DENSITOMETRIC MEASUREMENTS

Despite the fact that no provision to eliminate scattered light was employed, transmission readings in the normal working range, 10 percent to 100 percent could be made with considerable accuracy. However, for heavier lines from 1 percent to 10 percent, representing densities from two to one, scattered light could cause errors as indicated in the plot of densities against intensities (Fig. 4). To eliminate this type of error, a number of the conventional systems were investigated. It soon became apparent that any system depending upon lenses, whether used to project spectral lines onto slits or lines of light onto photographed spectral lines, was bound to suffer from scattered light. However, if a slit system could be made small enough so that it could be actually laid onto a spectral line, almost all of these errors should be eliminated. Such slits were made 0.0005″ wide and 0.045″ long (0.012 mm wide and 1.1 mm long). As used on the standard film projector one of these is fastened to a slide which moves the slit over the film and yet does not interfere with projection. This is done by sending the light up a tube at an angle by means of a mirror. Figure 5 shows the optical system. The slide mechanism stops against a screw driven by a small synchronous motor. This provides a mechanical sweep across the line making for accurate readings free of subjective errors.

The combination of a projector, a compensated amplifier and a line scanning slit proved so successful in the standard film densitometers that it seemed advisable to employ essentially the same system for plates. However, to prevent all tinkering and adjusting, it seemed advisable to build an amplifier operated entirely from alternating current. This was done by using a two-stage compensating type which gives extremely stable operation. It amplifies the output of a stable vacuum photo-cell, operated at low voltage, sufficiently to actuate a rugged large scale microammeter. To obtain constant illumination a large magnetic-type voltage regulator is employed to regulate the 115-v, 60-cycle input feeding the 250-w projection lamp. By balancing the load exactly, only a few tenths of a percent

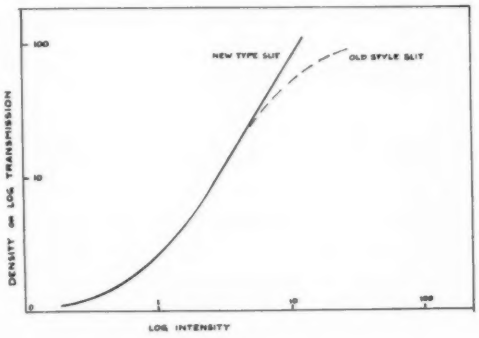

FIG. 4.

variation is found in densitometric readings for even large voltage fluctuations of the line. Elimination of optics between the spectral line and slit avoids inaccuracies caused by collection of dirt on lens surfaces out of focus, or misalignment. The motor-driven scanning mechanism is a vast improvement over hand scanning in that it eliminates one of the human variables. The motor driven scanning mechanism will repeat scanning the line until the operator stops the scanning operation by pushing a control button. This automatic repeating of a reading may be used to advantage for checking purposes.

On the front panel of the densitometer, just below the meter, are located two potentiometer control knobs. The one on the left is used to cause the meter to read zero. Before a plate is read, the operator scans a clean portion of the plate and adjusts the meter to read 100 percent transmission. This operation insures that the actual light transmission of a spectral line is read since light absorbed by the plate or film and emulsion is corrected for.

The scanning mechanism is mounted on a rotating table so that the slit may be aligned perfectly with slanting spectral lines if such are present. A control button on the front of the unit allows the operator to rotate the slit to any angle desired. The front leading edge of the slit shoe is in line with the slit opening. To align the slit with any line, the operator rotates the scanning mechanism until the front leading edge of the slit shoe aligns with the spectral line.

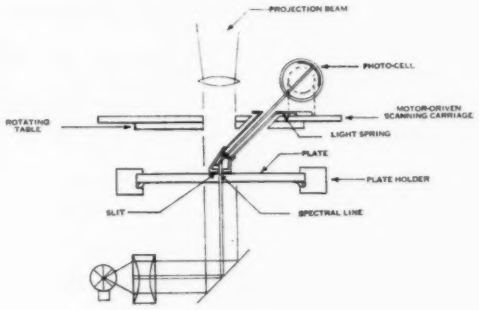

FIG. 5.

The standard slit width 0.0005″ opening has been found very satisfactory for all densitometric work or spectral lines. However, should the operator desire to use a different slit width, it is an easy task to insert a different slit into the slit scanning tube.

The Influence of Extraneous Elements on Line Intensity

III. The Effect of Anions*

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INVESTIGATORS seem to be in disagreement as to the effect which anions may produce on line intensity, and hence no generalizations can be made as in the case of the cations. Two Japanese workers[1] using a spark between the solution and electrode, reported that the intensity of zinc and magnesium lines remained constant with the use of either chlorides or sulfates. On the other hand, an excess of free hydrochloric acid weakened the *raies ultimes* of a large number of elements studied. Sulfuric acid had less effect, and excess nitric acid in the presence of nitrate salts produced no change. Thurnwald and Hultig[2] reported an opposite effect in the case of zinc lines. Gerlach and Schweitzer[3] in criticizing the latter's work proved that in an alloy of lead and tin the homologous pairs were unchanged from the original alloy after dissolving in hydrochloric acid, and also after dissolving in hydrochloric acid with an excess of nitric acid.

Triché[4] reported that an increase of free hydrochloric acid caused an increase in intensity of the lines of calcium and barium up to the point when the acid produced precipitation of the salts studied. The increase was explained as a function of conductivity and surface tension. Burke[5] on the other hand, reported that, using moderately large amounts of hydrochloric, nitric, and sulfuric acids present separately, no intensity change was observed in several lines of iron, nickel, manganese, and chromium.

Both Slavin[6] and Hess, Owens and Reinhardt[7] have pointed out that the acid portion of the test compounds affect the way in which the salt burns.

Duffendack, Wiley and Owens[8] have indicated that the chloride ion caused an increase in the intensity of the lines of sodium, potassium, magnesium, calcium and cadmium, whereas the sulfate and phosphate ions cause a decreasc in the intensities. However, the relative intensities were not affected in any case. A literature survey indicates that no investigation has been made of the effect on line intensity when only the anion is extraneous. This paper describes some trends which have been observed in the anion effect.

As a preliminary investigation the effect of the anion on the volatility of the salt has been shown by burning on carbon electrodes the same amount of barium in the form of different salts. The intensities of the barium lines on the various spectrograms are observed to be directly related to the boiling point of the salt or of its decomposition product. Figure 1 shows this effect by plotting the net galvanometer deflection-log time relationship using a rotating step-sector. Note that the curves of the most volatile salts lie near the top. Perhaps if the sample were completely ignited, the curves would be raised, since all of these are shown on the basis of constant exposure. The conclusion is well known and is presented here only as one of two general effects caused by the anions. First, the influencing of physical properties which may make for ease of burning, volatization and solubility. The second general effect is produced when the foreign anion present is combined with a metal already in the sample in large amount. Such considerations will be discussed now.

The insolubility of many salts outside the alkali group, which is to be avoided, limits the number of compounds that could be tested by the solution method. Hence, the solid sample method was used in preference to the solution technique.

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940. Parts I and II appeared in the Proceedings of the 6th and 7th Conferences, respectively.

[1] Y. Uzumasa and H. Ohuno, J. Chem. Soc. Japan **55**, 622 (1934).

[2] H. Thurnwald and G. F. Hultig, Zeits. f. anal. Chemie **76**, 260 (1929).

[3] W. Gerlach and E. Schweitzer, Zeits. f. anal. Chemie **77**, 213 (1929).

[4] H. Triché, Comptes rendus **200**, 1665 (1935).

[5] S. A. Burke, Trans. Faraday Soc. **33**, 309 (1937).

[6] M. Slavin, Eng. Mining J. **134**, 505 (1933).

[7] Hess, Owens and Reinhardt, Ind. Eng. Chem. Anal. Ed. **11**, 646 (1939).

[8] Duffendack, Wiley and Owens, Ind. Eng. Chem. Anal. Ed. **7**, 410 (1935).

Preliminary work showed that a special grade of calcium carbonate was a very satisfactory solid solvent giving very few spectral lines and containing practically no impurities save a trace of magnesium. Several elements were selected on the basis of their simple spectra and physical properties such as boiling point, ionization potential, etc. These are shown in Table I. Table II shows the lines that have been used in this study.

A large amount of a stock mixture was prepared containing calcium carbonate and pairs of test elements in concentrations which would give approximately equal intensities of the lines selected for the study. These stock mixtures were further mixed with the extraneous salts to be studied. The test metals were used in the form of oxides or carbonates, and the extraneous salts added either as calcium or barium compounds. The samples were well mixed by rolling in a ball mill for 6 hours. A standard was also made in the same way using calcium carbonate in place of the extraneous salt. Table III shows the method of preparation and the salts used. A change in the line intensity ratios from the value observed for the standard, was considered as caused by the presence of the foreign anion, the other conditions of the experiment remaining constant.

TABLE I.

ELEMENTS ALL AS OXIDES EXCEPT AS NOTED	EXCIT. POT.	ION. POT.	M.P.	B.P. COMPOUND	B.P. COMPOUND
Bi I	5.5–5.6	7.5 *ca.*	820	1900	1400
Cd I (as $CdCO_3$)	3.8	8.9	d. 500	900–1000	770
Pb I	4.4	7.4	888		1620
Sb I	5.3	8.0 *ca.*	656	1570	1440
Sn I	4.3	7.3	1127		2260
Zn I (as $ZnCO_3$)	4.0	9.4	$-CO_2$ 200 SnO 1800	1400	907

I un-ionized atom
Pair of elements studied: Bi–Pb Cd–Zn Sb–Sn

TABLE II. *Lines used in this study.*

Bi	Pb	Sb	Sn	Cd	Zn
2897.9° p	2802.0°	2718.9°	2706.5°	3080.8	3075.1
2938.3	2823.2°	2769.9°	2840.0° p	3252.5	3282.3 p
2989.0° p	2833.0° p	2877.9°	2850.6°	3614.4 p	3345.0 p
2993.3	2873.3°	3029.8	2863.2° p		
3024.6			3024.1		
			3175.0 p		

Line pairs used:
Pb–Bi Sn–Sb (Bi, Pb, Sn)–Sb Zn–Cd

° Lines used for working curves.

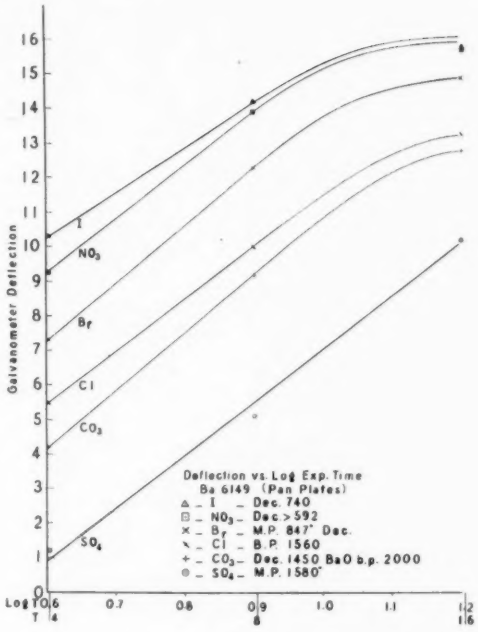

FIG. 1.

EXPERIMENTAL PROCEDURE

A large Hilger Littrow spectrograph was used in conjunction with a log sector for intensity measurements. The log sector of the usual type was rotated at 950 r.p.m. The lines studied were in the region 2700–3600A, Eastman 33 plates were used, and developed in Agfa No. 20 contrast developer for 3 minutes at 68°F. The spectroscopic grade of carbons made by the National Carbon Company were used. Direct-current arc operated at 5 amperes and 12 amperes was an excitation source. In most cases 10 ten-second exposures were made on the same sample. Where this time was changed, it was always compared to the standard samples which were exposed under the same conditions.

The plates were read by the aid of a scale magnifier. A piece of emulsion containing a log sector line was placed beside the scale as suggested by Wilhelm.[9] The use of this device greatly aided in obtaining consistent data. Observations were reproducible to within 0.2 mm.

The results observed from the plates were

[9] H. A. Wilhelm, Ind. Eng. Chem. Anal. Ed. **9**, 170 (1937).

TABLE III. *Table showing preparation of some samples.*

I. 12.000 g $CdCO_3$	II. 0.5146 g $PbCO_3$
0.480 g $ZnCO_3$	0.5448 g Bi_2O_3
49.80 g $CaCO_3$	48.94 g $CaCO_3$

Sb and Sn mixed in a similar way to give a greater dilution.
1.000 g extraneous salt
3.000 g stock base with Cd/Zn, Bi/Pb, or Sb/Sn
4.000 g sample well mixed in ball mill.
Extraneous salts used included: $Ca(OAc)_2$, $Ca_3(AsO_4)_2$, $Ca(ClO_3)_2$, $CaCl_2$, $CaSO_4$, $BaCO_3$, $BaBr_2$, BaI_2, $Ba(NO_3)_2$, $Ca(BO_2)_2$, $CaBr_2$, CaI_2, $Ca_3(PO_4)_2$, CaS, Li_2CO_3, Na_2CO_3.

studied in several ways, and some are shown in Table IV. The difference in actual line length between the value for the standard (carbonate alone present) and the value for sample containing the foreign salt (carbonate plus salt) for a single line is shown by the values of ΔL in Table IV. The larger the ΔL value, the more pronounced is the anion effect. It is to be noted that in most cases the sign is negative indicating repression, and the row headed $\Sigma(\Delta L)$ represents the summation of ΔL for all the lines observed.

Correlations of the data on the basis of the test element—internal standard difference in many cases covered up the effects since the two metals were frequently affected to the same degree.

From this part of the work we have concluded that those compounds which give rise to subhalide band spectra and are the most stable in the arc give the greatest effect. This includes calcium fluoride, calcium chloride, calcium chlorate after decomposition and barium bromide among the compounds tested. On the other hand, those compounds which decompose to give oxides most readily have the least effect. In this latter group of salts calcium borate, which exhibits considerable band spectra due to boric oxide, and calcium phosphate shows the greatest effect, but not comparable with the first three compounds listed in Table IV.

These conclusions raised the question as to how this change affects a working curve? A series of samples was prepared using calcium carbonate for a base, antimony oxide as an internal standard, and bismuth oxide, lead oxide and stannic oxide for test elements. The elements and compounds were selected on the basis of their ionization potential, boiling points, wave-lengths of lines used, and other similar properties which have been shown to be of importance as indicated in Table I. A diluting base, *Z*, which was made up of calcium carbonate and antimony oxide, was mixed in such a manner as to give a series of samples with graded concentrations as shown in Table V. Large amounts of these mixtures were prepared. In order to add an extraneous salt, the compound was mixed with calcium carbonate in proportion giving two percent and twenty percent

TABLE IV. *Table showing line length differences (ΔL) between standard sample (carbonate alone) and test sample (foreign anion present).*

	CaF_2	$CaCl_2$	$Ca(ClO_3)_2$	$Ca(OAc)_2$	$Ca_3(AsO_4)_2$	$Ca(BO_2)_2$	$Ca_3(PO_4)_2$	CaS	Na_2CO_3	$BaBr_2$
Pb 2802	−1.4	−0.5	−0.5	−0.5	−0.6	−0.6	−1.1	−0.4	−1.9	−0.4
$\Sigma(\Delta L)_{Pb}$ Four lines	−4.3	−3.3	−1.2	−1.9	−2.0	−1.7	−3.8	−1.6	−13.1	−1.4
Bi 3024	−2.9	−1.8	−1.7	−0.5	−0.3	+0.2	−0.5	−0.3	−7.3	−1.4
$\Sigma(\Delta L)_{Bi}$ Four lines	−8.5	−8.4	−7.0	−1.9	−1.0	+0.1	−2.9	−1.0	−25.2	−3.6

	CaF_2	$CaCl_2$	$Ca(ClO_3)_2$	$Ca_3(AsO_4)_2$	$Ca_3(PO_4)_2$	$CaSO_4$	CaS	$BaBr_2$	BaI_2	$Ba(NO_3)_2$
Cd 3252	−2.8	−3.0	−3.7	+0.1	−0.1	−0.3	−0.2	−1.6	+0.3	+0.8
$\Sigma(\Delta L)_{Cd}$ Three lines	−8.1	−9.5	−10.7	−0.6	−1.0	−1.1	−0.7	−4.6	+0.9	+2.0
Zn 3285	−3.2	−3.1	−3.9	−0.4	0.0	−0.8	−0.1	−2.4	+0.9	+0.4
$\Sigma(\Delta L)_{Zn}$	−6.7	−7.8	−7.8	−1.1	−0.5	−1.5	−0.7	−4.8	+0.9	+2.0

	CaF_2	$CaCl_2$	$Ca(ClO_3)_2$	$CaBr_2$	CaI_2	$Ca(BO_2)_2$	CaS	$Ca_3(PO_4)_2$	Li_2CO_3
Sb 3029	−4.5	−3.2	−2.2	−0.3	−0.5	−1.2	−0.4	−1.6	−4.4
$\Sigma(\Delta L)_{Sb}$ Four lines	−19.3	−12.0	−7.9	−3.4	−2.9	−5.2	−1.0	−5.6	−13.6
Sn 3034	−3.9	−2.5	−1.5	−0.5	−0.1	−1.1	−0.5	−1.8	−4.1
$\Sigma(\Delta L)_{Sn}$ Four lines	−17.5	−12.4	−7.5	−3.1	−1.3	−5.1	−2.2	−8.1	−17.7

TABLE V. *Method of sample preparation.*

SAMPLE NO.	% INT. STAND. Sb	% UNKNOWN Bi, Pb, Sn	METHOD OF PREPARATION
H	2.0	None	2% Sb as Sb_2O_3+$CaCO_3$ as a base material (*Z*)
G	2.0	0.0066	60 g *F*+120 g *Z*
F	2.0	0.02	60 g *E*+140 g *Z*
E	2.0	0.066	60 g *D*+120 g *Z*
D	2.0	0.2	60 g *C*+140 g *Z*
C	2.0	0.66	60 g *B*+120 g *Z*
B	2.0	2.0	60 g *A*+140 g *Z*
A	2.0	6.6	Mixed using 2% Sb, 6.6% Sn, Pb, Bi, all as oxides in $CaCO_3$

Extraneous salt preparation

I. 1.000 g extraneous salt
49.000 g $CaCO_3$

50.000 g extraneous salt 2%

II. 10.000 g extraneous salt 20%
40.000 g $CaCO_3$

50.000 g extraneous salt 20%

Extraneous salts—CaF_2, $CaCl_2$, $Ca(ClO_3)_2$, $CaBr_2$, CaI_2, $BaCO_3$, BaF_2, $BaCl_2$, and Na_2CO_3.
Equal parts of I or II are mixed with samples *A–H*.

and in certain cases other concentrations of the desired compound. Equal quantities of one of these "solid solutions" of anion and each of the series of samples (*A–H* Table VI) were mixed. This gives a series of samples in which the extraneous compound is present as one or ten percent, the antimony is present as one percent and the unknowns are 3.3, 1.0, 0.33, etc., percent.

Observations were made with barium salts and their trend was the same as the calcium. Since their use would possibly necessitate a correction for the barium atom, this group was dropped for the moment. A standard with no foreign anions present was made by mixing equal quantities of calcium carbonate and each of the samples *A–H*. All of the samples were burned in the arc under constant exposure conditions and developed in a procedure similar to that described in the previous section. The plates were read and the results have been correlated. Figures 2–5 indicate graphically the results that were observed. In nearly all cases, it is seen that one percent of the salt causes the line to be raised slightly above the standard, and ten percent affects it even more. Qualitatively calcium fluoride has the greatest influence, calcium chloride somewhat less, and the bromide and iodide least. Calcium chlorate also raised the intensity readings but did not give sufficiently satisfactory points to plot the data. The fluoride was studied at higher concentrations and figures showing the change here indicate that the curves seem to lie approximately parallel one above the other. As has been suggested, each set of graphs has been studied and the displacements of the line from the standard have been plotted against varying concentrations of the anion. These curves accompany the corresponding lines in each figure.

TABLE VI. *Samples in part A taken with lower electrode negative. Samples in part B taken with lower electrode positive. The letters opposite each element indicate the samples which showed the line. Both 5-amp. direct-current arc. A 12-amp. direct-current arc showed somewhat less effect.*

ELEMENT SAMPLES AND LINE	PART A			PART B			
	1% CaF_2	10% CaF_2	25% CaF_2	1% $CaBr_2$	10% $CaBr_2$	1% CaI_2	10% CaI_2
Bi *E–A* 2898	−5.4	−7.2	−11.8	+2.2	+2.6	+4.2	+2.4
Pb *E–A* 2873	+1.0	−5.0	−10.8	+0.2	+0.5	+1.9	+1.8
Sn *G–A* 2706	−2.3	−7.5	−12.2	+2.8	+2.3	+2.0	+2.6
Sb *H–A* 2769	−3.8	−12.7	−26.9	+4.3	+5.4	+5.5	+7.2
Ca *H–A* 2994	−1.9	+11.1	+25.3	+9.5	+13.7	+11.5	+6.3

Examination of these curves led to several observations and conclusions: (1) In most cases the effect is greatest for the higher concentrations of test element present, and diminishes for those of lower concentrations; lead and tin being affected the most. (2) The effect seems to approach a maximum which is in line with the observed excess effect of cations. (3) Calcium fluoride being more stable than the other halides in the arc, has the greatest effect, and the iodide decomposing easily has the least effect.

These observations raise the question as to which line did the fluoride affect? The internal standard, the unknown or both? Since the data is plotted $L_{unk}-L_{int\ std}$ and this difference is observed to increase it is possible that: (1) The intensity or the line length of the unknown is enhanced, (2) the intensity or the line length of the internal standard is depressed, (3) or one of several possible combinations of the two above cases.

To determine which of these possibilities was occurring, all the line lengths for a given wavelength in a given series were totaled. Repre-

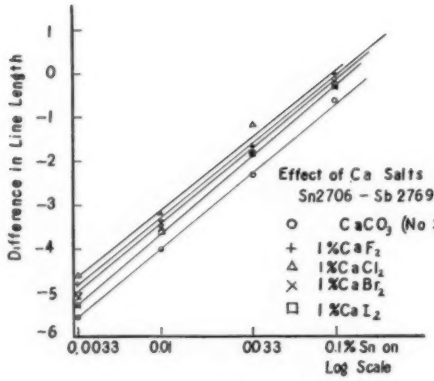

FIG. 2.

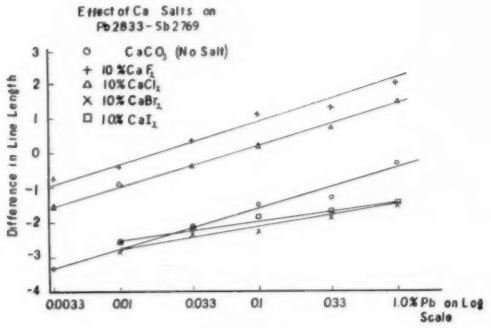

FIG. 3.

sentative results under different conditions are tabulated in Table VI. The values indicated are changes from the standard carbonate, and a minus value shows weakening of the line, and a positive value shows strengthening. These results indicate in a more general way what has already been said in regard to the nature and quantity of the anion. More significantly it shows that antimony is affected more than lead, tin, or bismuth. In a way it is unfortunate that an element should have been selected for an internal standard which varies more than the "unknown" elements. However, in the light of the previous observations that the effect seemed to increase with increasing concentration of the unknown, it would be possible or likely that nearly any other metal present as an internal standard at one percent may be affected more than the unknown at a lesser percent. The standard element is present as a total of eight percent in 8 samples and the test element is present as 4.77 percent in 7 samples.

The B part of Table VI, indicates another interesting point. The samples with one and ten percent calcium iodide and calcium bromide show an enhancing effect instead of repression. During the mixing process these samples changed in color indicating that the calcium iodide and bromide salts reacted with the metal oxides forming antimony, bismuth, lead and tin iodides and calcium oxide. Since the boiling points of the iodides are lower than the metal oxides, this would explain the enhancement.

A plausible explanation of this repression by calcium fluoride and the other halides, rests in the explanation of the similar effects of sodium salts. The potential necessary to excite calcium fluoride to give the subhalide band spectra is about 2.1 volts, a voltage similar to that required in the case of atomic sodium. One difference to be noted, however, is that the amount of calcium fluoride required for the repression to become constant is much greater than the amount of sodium. A larger amount of calcium fluoride is required since it partially breaks down to give atomic spectra whose effect is to increase the calcium line intensity.

It should be pointed out that these observed effects will not cause the usual trouble as in the case of the sodium, etc., in spectrographic analy-

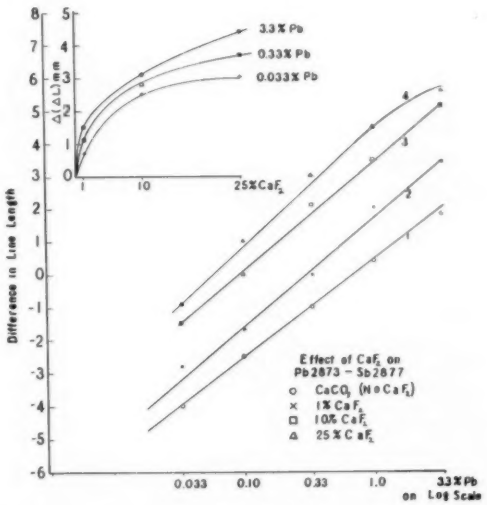

FIG. 4.

sis. In most cases, samples are treated so as to convert them all to a common acid radical, sulfate, nitrate or chloride. In the case of the latter this would be corrected for when making up the working curves from known materials. Fluorides, bromides and iodides are not frequently encountered in routine quantitative spectrographic analysis.

Summary and Conclusions

The results of this research may be summarized:

(1) In a given series of compounds of different anions but common cation the line intensity of the cation is greatest for those compounds or their decomposition products having the lowest boiling point.

(2) When anions are present as an extraneous substance, those which tend to give subhalide band spectra show relatively greater effect on the line intensity than do those compounds tending to break down to calcium oxide.

(3) Of the four halogen salts studied calcium fluoride shows the greatest effect, followed by calcium chloride. Calcium bromide and calcium iodide do not lend themselves to good tests because chemical reaction in the sample caused them to be anomalous from the standard.

(4) The repression of the line intensity generally becomes greater for larger concentrations of the elements being measured.

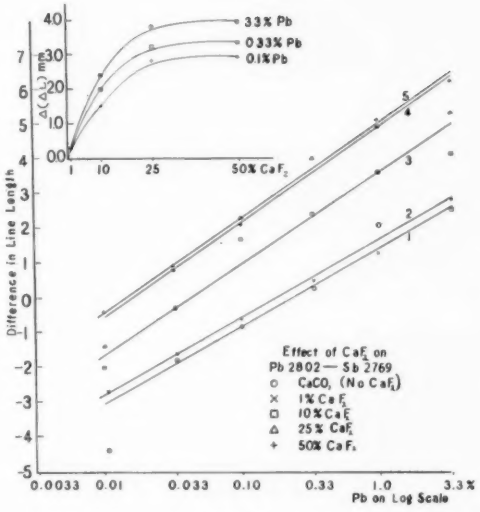

Fig. 5.

(5) The repression of line intensity approaches a maximum with increasing concentration of calcium fluoride.

(6) It is shown that this effect may be caused by the lower energy necessary to excite the band spectra of calcium fluoride than the lines under consideration.

(7) The conclusions made are in line with observations and explanations for the effect of the third or extraneous atom when it is a metal.

A Concave Grating Photoelectric Spectrophotometer*

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AND

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PRIOR to the design and development of the instrument to be described, preliminary studies were made of the use of concave replica gratings for the purpose of obtaining substantially monochromatic light for photometric analysis. Concave grating spectrometers of the Rowland type which are commercially available were used. A suitable exit slit, absorption cell holder and barrier-layer photo-cell replaced the conventional eyepiece. These were rigidly attached to the movable arm of the Rowland mount opposite the grating and measurements were made in the first-order spectrum. A tungsten incandescent source, operated on a constant voltage transformer, served as the light source. With this improvised equipment the feasibility of using such a combination as a spectrophotometer was clearly demonstrated in both of our laboratories. The favorable results obtained, as well as the problems and difficulties encountered in these preliminary surveys, led to the development of the present instrument.

THE SPECTROPHOTELOMETER AND ACCESSORIES

The monochromator of the Spectrophotelometer† is essentially a modified Eagle[1] mount. The essential features of the instrument are shown schematically in Fig. 1 to emphasize the mechanism by means of which substantially monochromatic light is made available for investigations on the absorption of light. Light which enters the first slit S_1 is reflected by the front aluminized mirror M through a "light tunnel" to the grating G. The light is diffracted in various directions in accordance with the grating theory, but a particular diffracted beam returns slightly above the incident beam, passing through the exit slit or second slit S_2 and through the absorption cell A to the photo-cell Ph.

The wave-length of the diffracted beam which passes through the slit S_2 is determined by the angle θ_1 and is controlled by the crank C through the gear mechanism. When the instrument is in adjustment, the middle wave-length of the diffracted beam which emerges from the second slit is shown by the wave-length indicator W. As the crank C is turned, the center O of the Rowland circle rotates about the fixed point O_1 and the grating slides on the fixed ways Y and turns with respect to the point O_1 so that the angle θ_1 varies. For all wave-length settings the Rowland circle passes through the point O_1 and is tangent to the center of the concave surface of the grating. The extreme positions of the grating for the first-order spectrum are O_2 for long wave-lengths and O_2' for short wave-lengths. In view of the properties of the concave grating and the type of mount, a diffracted beam is always in focus at the slit S_2 located at the point O_1. Since nearly uniform dispersion is maintained at the exit slit regardless of the spectral region isolated, exit slits of constant width are used.

The primary adjustment and calibration for wave-length of the instrument are made in the factory. These adjustments are made by altering the lengths of the arms X_1 and X_2 and by manipulating the knurled nuts on the grating support K. It is expected that these major adjustments will remain fixed indefinitely so that the user need only verify the calibration. The anti-backlash spring F is under compression. Consequently, in adjusting the instrument to a particular setting of wave-length, the crank C must always be turned in a clockwise direction—that is, from lower wave-lengths to higher wave-lengths.

A front view of the instrument is shown in Fig. 2. Attention is called to the screw for the adjustment of the entrance slit and the dial on the left face of the instrument which indicates the width of the entrance slit on a 0.1-mm scale. The slit is bilaterally adjusted for width. The crank for making wave-length adjustments is

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940.

† Trade mark registered, U. S. Patent Office.

[1] A. Eagle, "New mounting for concave grating," Astrophys. J. **31**, 120 (1910).

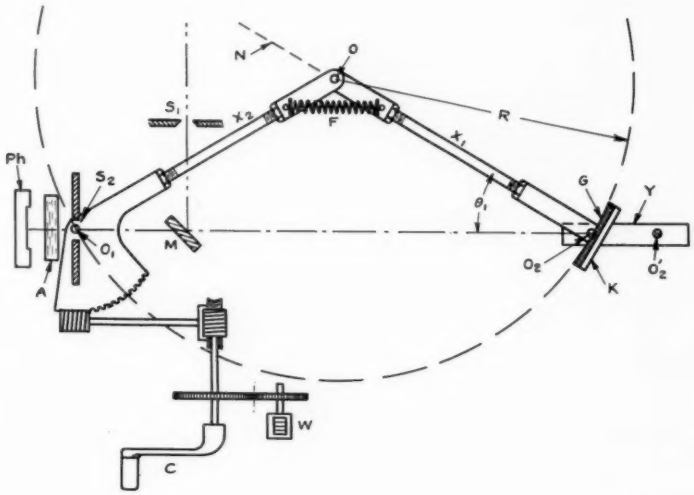

FIG. 1. Schematic diagram of the monochromator.

shown on the right and the wave-length indicator is shown set for 328 millimicrons. The absorption cells, which hold about 2 milliliters of solution and which have fused Corex windows, are shown in the cell carriage. The cell on the left contains the clear solvent, while that on the right contains the solution on which measurements are to be made. These absorption cells are made of optically ground and polished glass and are optically flat to within a few wave-lengths of light. The thickness of the absorption path is maintained to a tolerance within 0.5 percent.

On the top of the instrument and near the front there is mounted a viewing tube. This consists of an eyepiece, cross hairs and a total reflecting prism. This tube may be lowered to intercept the diffracted light beam, in which case the spectral region isolated is brought to a focus in the plane of the cross hairs. The plane of the cross hairs when in the lowered position is the same distance from the grating as the exit slit. Consequently, when the cross hairs are properly adjusted, the middle wave-length of the spectral region isolated falls at the intersection of the cross hairs. This device is not merely a great convenience in the primary calibration of the instrument; it is, in fact, essential to the maintenance of accuracy of the instrument, since it permits immediate checking of the wave-length scale. After the primary calibration has been established, final calibration (even after shipment) is effected by rotating the grating slightly about a vertical axis. For example, if the 546-millimicron line of mercury is set on the center of the cross hairs by a slight rotation of the grating about the vertical axis, the wave-lengths of other spectral lines will agree with the wave-length setting to within ± 1 millimicron.

Although exit slits of various widths may be used, four are supplied with the instrument. These have nominal spectral widths of 20, 10, 5 and 2.5 millimicrons. Since the dispersion is approximately 4 millimicrons per millimeter, the actual widths range from 5 mm to 0.6 mm. The slits are 13 mm in length. They are inserted in a

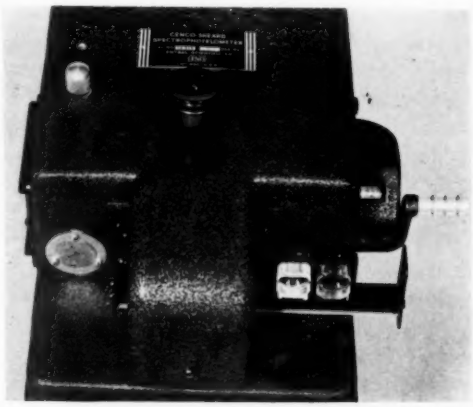

FIG. 2. Front view of Spectrophotelometer.

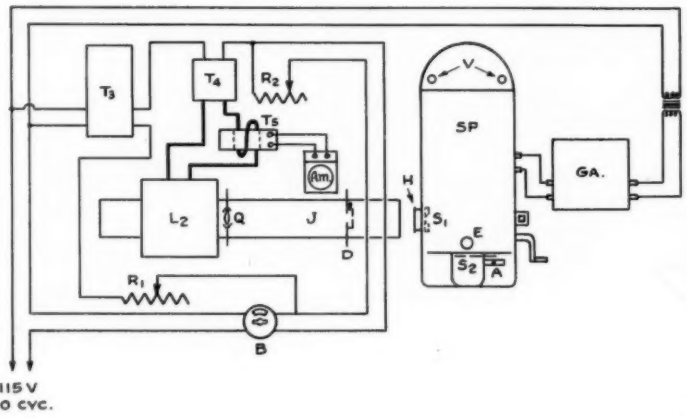

FIG. 3. Schematic diagram of Spectrophotelometer and accessories for range 325 to 750 millimicrons: L_2, incandescent source; T_4, step-down transformer; T_3, constant voltage transformer; R_1 and R_2, variable resistors; B, three-position rotating snap switch; T_5, current transformer; Q, quartz lens; D, iris diaphragm; S_1, entrance slit.

slot immediately in front of the absorption cells and click into position as the slide is moved laterally.

The barrier-layer photo-cell used in the Spectrophotelometer is directly connected to a box type galvanometer. The galvanometers have a sensitivity within the range of 1.2 to 1.5×10^{-9} ampere per millimeter deflection. The coil resistance of the instrument is about 450 ohms and the critical damping resistance is of the order of 10,000 ohms. The reference line of the galvanometer is projected on a scale 100 mm long. The smallest division indicated is 1 mm. The instrument may be read to 0.2 mm. The characteristics of the photo-cell indicated by the manufacturer are such that approximately 2×10^{-6} lumen of energy is required for 1 mm deflection on the galvanometer. As will be shown later, a linear response between light intensity and galvanometer deflection obtains over the range of wave-lengths from 325 to 750 millimicrons.

A schematic diagram of the arrangement of the Spectrophotelometer and accessories for making readings between 325 and 750 millimicrons is shown in Fig. 3.

THE SPECTRAL REGION ISOLATED

Reference has been made to exit slits of nominal widths of 20, 10, 5 and 2.5 millimicrons. This terminology is used since it is obvious that the spectral region isolated by an exit slit depends on the width of the entrance slit as well as that of the exit slit. It is customary to compute the physical width of an exit slit which will pass a given band of light on the basis of an entrance slit having zero width, hence the designation "nominal slit width." One may also define the spectral region isolated by a particular exit slit for zero entrance slit as the "nominal wave-length band." Obviously, as the entrance slit is opened, two side bands of energy will extend the spectral region isolated on each side of the nominal wave-length band. These side bands contribute energy in wave-lengths contiguous to the extremes of the nominal wave-length band, but the energy rapidly falls to zero at the extremes of the total spectral region isolated.

In this instrument the total width, in millimicrons, of these side bands—that is, the width of the band on the side of the short wave-length plus the width of the band on the side of the long wave-length—is equal to four times the width of the entrance slit in millimeters. Consequently when the 5-millimicron exit slit is used with a 0.5-mm entrance slit, the total spectral region isolated will be 7 millimicrons. Since the light energy at the extremes of the spectral region isolated is zero, the major portion of the energy lies in the 5-millimicron band. A comprehensive analysis of the effect of width of entrance slit on the spectral region isolated as well as the effect on transmission measurements has been published recently by Hogness and his colleagues.[2]

[2] T. R. Hogness, F. P. Zscheile, Jr. and A. E. Sidwell, Jr., "Photoelectric spectrophotometry. An apparatus for the ultra-violet and visible spectral regions: its construction, calibration, and application to chemical problems." J. Phys. Chem. **41**, 379–415 (1937).

Stray Light

A light-proof metal housing completely encloses the optical system and associated working parts of the instrument. In addition, the incident and diffracted beams pass through a light tunnel which further protects the exit slit. The inside of the light tunnel contains numerous baffles and the entire inner surface is covered with a soft, black, light-absorbing material. Notwithstanding these and other features, additional precautions are necessary to eliminate stray light from measurements at the extreme ends of the spectral region. This stray light arises from two different causes but both may be effectively eliminated.

When the instrument is set for measurements below 410 millimicrons, the grating and its holder are substantially normal to the incident beam. As a result, stray light of longer wavelengths which is scattered through the light tunnel reaches the exit slit. Although this stray light is sufficient to show a faint haze in the eyepiece when the instrument is set below 390 millimicrons, it may be eliminated by use of a filter which absorbs in the region above 410 millimicrons. The filter is mounted in the holder immediately in front of the entrance slit. Transmission measurements made with the filter in position will be substantially free of stray light effects, as will be indicated later.

In the red end of the spectrum, above 650 millimicrons, there is another stray light effect. In addition to the effective scattered radiation, the second-order spectrum is superimposed on the first. However, the undesirable energy from both of these sources may be absorbed by the use of a filter which does not transmit light in the region below 600 millimicrons.

Stray light of one percent or less in the beam passing through the solvent (I_0) may or may not have appreciable effect on the transmittancy of a solution. The effect is negligible in the event that the stray light is absorbed to the same extent as the light in the isolated spectral region. In other cases the error introduced in measurements of the transmission may be several percent. Complete analysis for stray light for a given absorbing material involves the summation of effects for the entire spectrum for each wave-length setting. However, a theoretical case* is of interest if for no other reason than that it illustrates the nature of the problem.

Suppose that the stray light involved in the transmittancy measurement at a particular wavelength may be divided into two parts, one part which is absorbed by the substance to the same extent as the spectral region isolated and a second part which is either not absorbed at all, or is entirely absorbed, or, again, is only partially absorbed by the substance. On the assumption that the light intensities are proportional to a galvanometer deflection, if the second component contributes x millimeters to the deflection I_0 for the clear solvent, then the deflection I for the solution will be too large by some fraction of x, and the true transmittancy is given by

$$T=\frac{I-fx}{I_0-x}, \tag{1}$$

where f may have values ranging from 1 to 0. If T' is the apparent transmittancy for the solution —that is, I/I_0—this equation may be solved for the fractional error in the transmittancy. Or

$$\frac{T'-T}{T}=\frac{x}{T}\frac{(f-T')}{(I_0-x)}. \tag{2}$$

From this relationship it is clear that the error in the transmittancy measurement is 0 when x is 0 or when f equals T'. This latter condition amounts to saying that the second component is absorbed to the same extent as the region isolated. For values of f greater than T', the error in the transmittancy will be positive; for values of f less than T' the error in transmittancy will be negative. Equation (2) also indicates that the error in the transmittancy may be very great if the transmittancy of the solution is small.

A number of tests have been made to determine the magnitude of the stray light in the instrument. Molecular extinction coefficients have been measured and compared with accepted values, the transmission values of filters at various wave-lengths have been checked with the measurements on other types of instruments, and an analysis has been made with a spectrograph

* This problem has been treated by Hogness and his colleagues, although in a different manner.

using the instrument as a monochromator. In Table I are shown comparative transmission values for a Corning H. T. Yellow Beta 4 filter. The quantities in column 2 are certified transmission values on National Bureau of Standards Test No. 89220. Column 3 shows the uncertainty in these measurements. Columns 4 and 5 show corresponding measurements of this filter made with a Spectrophotelometer, with and without appropriate filters mounted before the entrance slit. These data were obtained with a 1-mm entrance slit. Two exit slits were used—a 5-millimicron slit for the range 400 to 660 millimicrons, and a 10-millimicron slit below 400 and above 660 millimicrons. Four filters were used, as shown by the asterisks in column 4. For practical purposes the use of filters between 420 and 650 millimicrons appears unnecessary. These tests and other experiments indicate that the stray light is not greater than 1 percent of the incident energy at any setting within the range of the instrument and much less throughout most of the spectrum.

Calibration of the Instrument

In Fig. 4 is shown a transmission curve for a didymium filter. The 2.5-millimicron exit slit was used and the entrance slit was adjusted to the smallest value consistent with satisfactory galvanometer deflections throughout the range.

Table I. *Data obtained in the examination of the Spectrophotelometer for stray light.*

Wave-Length Milli-microns	Values of T (National Bureau of Standards)	Uncertainty in T (N.B.S.)	Transmission (I/I_0)	
			With Filter	Without Filter
390.0	0.021	±0.002	*0.025	0.032
404.7	0.0172	±0.0008	0.0197	0.022
420.0	0.016	±0.001	*0.0187	0.021
435.8	0.0221	±0.0004	0.0227	0.025
471.3	0.077	±0.001	0.0788	0.079
491.6	0.153	±0.003	*0.156	0.148
501.6	0.201	±0.003	0.202	0.203
520.0	0.309	±0.004	0.310	0.309
530.0	0.372	±0.004	0.373	0.367
546.1	0.475	±0.003		0.474
560.0	0.550	±0.004		0.545
578.0	0.633	±0.003		0.637
587.6	0.664	±0.003		0.659
600.0	0.697	±0.004		0.697
620.0	0.730	±0.004		0.727
640.0	0.745	±0.004		0.745
660.0	0.751	±0.005	*0.752	0.747
690.0	0.752	±0.005	0.753	0.717
720.0	0.744	±0.006	0.746	0.645
750.0	0.727	±0.006	0.733	0.573

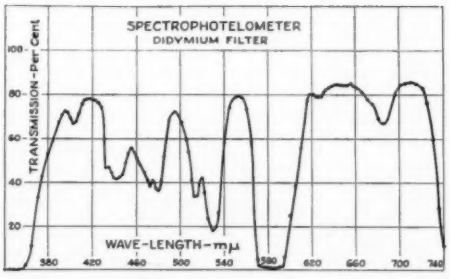

Fig. 4. Transmission curve for a didymium filter.

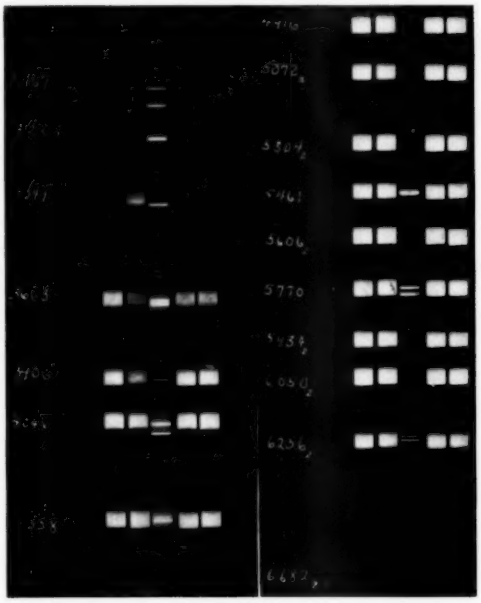

Fig. 5. Spectrogram demonstrating agreement between Spectrophotelometer setting and mercury arc lines.

The absorption bands at about 475 and 525 millimicrons are definitely resolved. The points shown are individual readings and no attempt was made to analyze the structure at a number of other interesting regions such as at 435 millimicrons. Absorption minima occur at 403, 441, 473, 480, 514, 530, 585 and 685 millimicrons. The position of these minima on the wave-length scale may be reproduced on various instruments to within ±1 millimicron. To do this the identical filter must be used and the spectral region isolated must be the same for corresponding transmission measurements. Under these conditions

the transmission values for the filter are reproducible on various instruments. The variations in the observations at a particular wave-length will depend on the slope of the transmission curve at the point. Where the curve is flat, reproducibility is within 1 percent.

Possibly a better demonstration of the accuracy of calibration of the instrument is shown in Fig. 5. This spectrogram was obtained by using a tungsten light and by focusing the spectral region isolated by the monochromator on the slit of a spectrograph. A number of exposures were made at various wave-length settings corresponding to either first- or second-order mercury spectral lines. In all, some sixty exposures were made to secure a set of four readings for each wave-length setting. In addition, light from a mercury arc was used to secure accurate wave-length indications. The width of the bands corresponds to a spectral region of approximately 6 millimicrons. The accuracy of the wave-length setting is seen to be within ± 1 millimicron with the possible exception of settings near 325 millimicrons.

The Barrier-Layer Photo-Cell

Much has been said concerning the use of barrier-layer cells for the measurement of light intensities. One writer has referred to the "fatigue effects, instability and nonlinearity which characterize barrier-layer photo-cells." That fatigue occurs, especially at high levels of intensity, is well known. Such a characteristic, however, does not necessarily affect transmission measurements since the result obtained is a ratio of two readings taken almost simultaneously. The impression that it is not possible to obtain a linear response from a barrier-layer cell undoubtedly arises in part from the use of these devices in filter photometers. Unless the absorption band for a given solution is rather broad in comparison with the transmission band of the filter used, calibration curves of solution concentrations *versus* the logarithm of transmission values are usually nonlinear. Since nonlinear results of this sort are obtainable on solutions

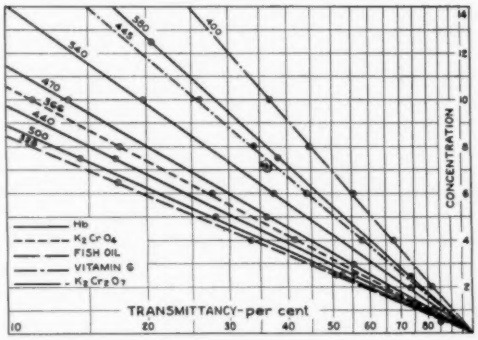

FIG. 6. Calibration curves showing linear response of photo-cell.

which obey the Bouguer-Beer law, the conclusion is reached that the cell is responsible for the results obtained.

Whether the difficulty has been eliminated by using a narrow spectral region or by the use of low intensities of light, or whether the result is a combination of these two effects, the calibration curves shown in Fig. 6 indicate that the barrier-layer cell is capable of giving a "linear response." The solutions used were taken at random to secure data at various spectral regions. To simplify the diagram, the concentrations were reduced to an arbitrary scale. Water was the solvent used for the hemoglobin, potassium chromate, potassium dichromate and vitamin *G*. The fish oil was dissolved in naphtha. With the exception of the curve at 366 millimicrons, the points indicated are single observations. Each point on the latter curve is the average of ten individual transmittancy measurements and the line was drawn to conform to the molecular extinction coefficient for potassium chromate rather than through the observed points. For the different curves, various entrance and exit slit widths were used.

It is not necessary to suggest possible applications of such an instrument. It is sufficient to say that the Spectrophotelometer will be a valuable addition to the equipment of laboratories interested in photometric analysis.

The Establishment of Precise Spectrophotometric Constants for Hemochromogens and Cytochrome C upon an Iron Basis, and the Analysis of the Cytochrome C Spectrum*

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FOR present purposes spectrophotometric constants may be defined in terms of the *extinction coefficient, ϵ, at millimolar concentration, for a depth of solution of 1 cm, in spectral regions characteristic of the solution measured (maxima or minima of absorption), and under reproducible conditions, which include calibration by use of a reproducible standard,[1] a specified spectral interval, and a sufficient number of analyses upon independent preparations of the substance studied.* The reference concentration of 1 mM per liter was chosen for convenience, and in these studies 1 mM refers to 1 milliequivalent of iron. Our constants can be converted to molar extinction coefficients, in terms of iron, by multiplying them by the factor 10^3.

In establishing spectrophotometric constants for hemoglobin and its close derivatives, the determination of oxygen capacity by the method of Van Slyke and Neill[2] was used as an independent analytical procedure, and advantage was taken of the ease of quantitative conversion of these hemoglobin derivatives to cyanmethemoglobin, a relatively stable compound with characteristic spectrum providing a valuable accessory standard.[3] Reliable constants could not be established in earlier studies of hemochromogens,[4] (which are typified by such compounds as dipyridinoferri or ferroporphyrin and the naturally occurring catalyst of cellular oxidation-reduction processes, cytochrome C), since such substances do not form reversible compounds with oxygen, making unavailable oxygen capacity measurement as an independent technique. In solution with cyanide ferrihemin and many ferrihemochromogens (but not oxidized cytochrome C) have been found by the writer[5] to yield absorption spectra very similar to that of cyanmethemoglobin, but, without an independent method of standardization, it was thought unjustifiable to consider interchangeable the constants upon cyanide derivatives of hemins with that of cyanmethemoglobin. Under these circumstances it became necessary to turn once again to the independent determination of iron as a basis for establishment of precise spectrophotometric constants. Frankly, this was a last resort, since even in the best hands[6] the error of iron analyses upon hemin derivatives and cytochrome has been high in comparison with the error expected in precise spectrophotometry.[1,2]

By suitable modification of a new method,[7] the writer has succeeded in determining the iron in hemin and cytochrome C preparations with a precision equal to our best performance in the measurement of the absorption spectra of hemoglobin and close derivatives.[1,2] The method is sensitive to the presence of 1 gamma of iron per cc of solution, and 10-mg samples of cytochrome C preparations of about 50 percent purity (0.43 percent Fe[8] assumed for the pure compound) were sufficient for accurate analysis. A brief outline of the essential steps of the method follows: (a). Iron is freed from the organic

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940.

† Fellow of the John Simon Guggenheim Memorial Foundation at the Department of Physiological Chemistry, The Johns Hopkins School of Medicine. Part of this work was done during tenure of the fellowship.

[1] D. L. Drabkin and J. H. Austin, J. Biol. Chem. **98**, 719 (1932).

[2] D. D. Van Slyke and J. M. Neill, J. Biol. Chem. **61**, 523 (1924).

[3] (a) D. L. Drabkin and J. H. Austin, J. Biol. Chem. **112**, 51 (1935–36); (b) D. L. Drabkin, "Spectroscopy in science and industry," *Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications* (John Wiley, New York, 1938), p. 94.

[4] D. L. Drabkin and J. H. Austin, J. Biol. Chem. **112**, 89 (1935–36).

[5] D. L. Drabkin, J. Biol. Chem. **123**, xxxi (1938); *Proceedings of the Seventh Summer Conference on Spectroscopy and Its Applications* (John Wiley, New York, 1940), p. 116.

[6] R. Hill, Proc. Roy. Soc. London **B107**, 205 (1930); R. Hill and D. Keilin, Proc. Roy. Soc. London **B114**, 104 (1933).

[7] O. Schales, Personal communication to the writer; W. Lintzel, Zeits. f. ges. exp. Med. **86**, 269 (1933); G. Barkan and B. S. Walker, J. Biol. Chem. **131**, 447 (1939); **135**, 37 (1940).

[8] H. Theorell and Å. Åkesson, Science **90**, 67 (1939).

TABLE I. *Spectrophotometric constants, ϵ(c=1 mM per liter, d=1 cm), upon 4 independent preparations of cytochrome C.*

WAVE-LENGTH mμ	CONSTANTS	S.D.*	$\frac{\epsilon\lambda_{552}}{\epsilon\lambda_{535}}$ $\frac{\epsilon\lambda_{522}}{\epsilon\lambda_{535}}$
552†	26.14	0.22±0.08	3.53
535‡	7.41	0.06±0.02	2.09
522†	15.47	0.10±0.04	

* S.D., standard deviation = $[\Sigma d^2/(n-1)]^{\frac{1}{2}}$. The figures after the ± represent the standard error of the standard deviation, or S.D./$(2n)^{\frac{1}{2}}$.
† Maxima; spectral interval =1.5 to 2 mμ.
‡ Minimum; spectral interval =1.5 to 2 mμ.

complex by treatment with dilute NaOH and H_2O_2 (Superoxol). (b). The solution is freed of H_2O_2, and *p*H adjusted to 4.2–4.3 by means of HCl and ammonium acetate. (c). The iron is reduced by means of ascorbic acid, and orthophenanthroline added, forming slowly a relatively stable, rose-colored complex of ferrous orthophenanthroline. (d). After completion of the reaction, the light extinction of the colored complex is determined spectrophotometrically or photometrically. Iron standards, prepared from pure iron wire, are run simultaneously. Redistilled distilled water is employed, and the extinction caused by the very slight yellow color present in the cytochrome C solutions (but not in the iron standards), before the addition of ascorbic acid and phenanthroline, is determined, and serves as a precise, small correction factor.

The proper photometry of the colored solution is believed to be the most important step in the method. By means of visual spectrophotometry, the value of ϵ (c=1 milliequivalent of Fe, d=1 cm), at wave-length 500 mμ (the maximum) was found to be 11.05. Particularly satisfactory results were obtained by means of photoelectric, filter photometry, using a photometer of new design, with photo-cell chosen primarily because of its characteristic maximum sensitivity in the blue spectral region (to be described later). Results were based upon averages of determinations at two wave-length intervals, 485 mμ and 535 mμ, the respective filters being (1) Wratten filter No. 75η (blue-green), plus a 1-cm layer of 0.8M $CuSO_4$ solution, and (2) Wratten filter No. 62 (mercury green), plus a 1-cm layer of 0.8M $CuSO_4$ solution. Upon ferrous orthophenanthroline, the extinction data yielded by the new filter photometer were virtually identical with that obtained by precise, visual spectrophotometry. This is in marked contrast to the type of data yielded by the usual form of filter photometer employing a barrier-layer photo-cell, such as the Evelyn apparatus.[9]

Basing the concentration of total pigment upon the determination of iron, ϵ (c=1 mM per liter, d=1 cm) values for dipyridino ferroporphyrin were 31.0, maximum at wave-length 558 mμ, 9.2, minimum at 540 mμ, and 16.4, maximum at 525 mμ, using a very narrow spectral interval of 1.5 to 2 mμ. As far as I have been able to ascertain, these are the highest constants which have been reported for the above "hemochromogen." The pigment solution was made up from the same α-chlorohemin, prepared by the writer from washed dog erythrocytes, and used in the earlier studies of Drabkin and Austin.[4] Similarly, with concentration based upon iron content, constants presented in Table I were established upon 4 independent preparations of cytochrome C.*

Having established the constants, concentration could, of course, be calculated from the extinction values upon the pigment solutions, treated as "unknowns." The concentration of iron so calculated agreed within 0.5 percent with that determined directly. Such an agreement is considered extraordinary in work of this type. It is also of interest to point out that the spectrophotometric determination of iron as ferrous orthophenanthroline is both more sensitive and considerably more accurate than its determination by quantitative emission spectroscopy by the usual techniques.

The visible and ultraviolet absorption spectrum of reduced cytochrome C has been determined, and the absorption curve analyzed into component units by the method introduced by the writer in the analysis of spectra of hemo-

[9] K. A. Evelyn, J. Biol. Chem. **115**, 63 (1936).

* One of the preparations was very kindly supplied to the writer by Dr. Hugo Theorell of the Nobel Biochemical Institute, Stockholm, Sweden. The method of preparation was that described in Theorell's original paper [Biochem. Zeits. **285**, 207 (1936)]. Dr. Theorell's analysis by an independent method was 0.287 percent iron, while the writer's analysis was 0.292 percent iron, or a purity of 67.9 percent for the cytochrome C preparation. The other cytochrome C preparations were made to specification, by the method of Keilin and Hartree [Proc. Roy. Soc. London **B122**, 298 (1937)], at the Wilson Laboratories under the supervision of Dr. David Klein.

globin derivatives.[3,5,10] Maxima in the spectrum are located at wave-lengths 552, 522, 415, 352, 313, 273.5, 248, and 224. When these wave-lengths are converted into frequency units, such as wave-number, ν (and, for convenience $\nu \times 10^{-2}$ is used), it becomes obvious that except for the two maxima in the green region, all the other maxima are at equal distances from each other. The positions of the integrally related maxima (centers of component bands of one series) are predictable by the simple expression $n.40$, where n is a simple integer, here $=6, 7, 8, 9, 10$, or 11, and 40 is the fundamental $\nu \times 10^{-2}$ value, or the location of the first band in the series. This series was expected in the spectrum of cytochrome, since it had been demonstrated in the spectra of hemoglobin derivatives.[3,5,10] The remarkable fact, however, is the presence of maxima in the reduced cytochrome C spectrum at wave-lengths 313, 248, and 224. These maxima, belonging to components 8, 10 and 11 of the series, were not present in the hemoglobin derivatives studied, although the components were graphically demonstrated in the writer's analysis. It was thus particularly pleasant to have the cytochrome spectrum. As in the case of the hemoglobin derivatives, the complex absorption curve can be expressed mathematically as a summation of individual curves or bands, whose shapes are those of normal probability curves. The individual bands of the series are probably electronic in nature, and are thought to be an expression of the same general structure, iron in coordinated linkage.

[10] D. L. Drabkin, J. Biol. Chem. **119**, xxvi (1937).

The Measurement of Fast Reactions by Absorption Spectrophotometry and Its Application to Respiratory Enzyme Kinetics*

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THIS paper describes a technique which has been developed for the study of rapid chemical reactions using a recently constructed high speed automatic recording absorption spectrophotometer.[1,2] A brief description of the application of this method to the study of the kinetics of the respiratory enzyme horseradish peroxidase is also given.

DESCRIPTION OF APPARATUS

The possibility for the measurement of rapid reactions involving changes of absorption arises from the fact that this spectrophotometer automatically compares the transmission of the solution and solvent twenty times per second, and records the optical density of the solution relative to the solvent every time. In ordinary operation of the instrument a plot of optical density against wave-length is obtained, but for purposes of kinetic investigations the spectrophotometer is set at any desired wave-length and a plot is made of optical density against time.

The details of construction and operation of the spectrophotometer have been given elsewhere[2] and only the essentials necessary for this report will be noted here. In the comparison of the transmissions of the solution and solvent a disk containing a constant opening and a variable opening is caused to rotate in front of the entrance slit of the dispersing system, as shown in Fig. 1. Synchronized with the motion of the disk is the oscillation of a biprism, placed close to the exit slit, directing the beam through the solution while the constant opening of the disk is in front of the entrance slit, and then through the solvent during the passage of the variable opening before the slit. The response of an electron multiplier to the light transmitted by the solution is registered as a voltage across a "memory" condenser. This unit operates in such a way that at the moment when the intensity of the comparison beam, which is continuously reduced by the variable opening of the disk, is equal to the intensity of solution beam, a spark is fired, and the value of the optical density is recorded. The optical arrangement of the spectrophotometer produces a linear relation between the length of the disk opening and the intensity of the beam.

The recording process consists of a spark punching a hole in a sheet of graph paper wrapped around a drum which rotates on the same shaft as the disk (Fig. 1). The spark point, whose position is indicated by an arrow in Fig. 1, is placed close to the drum, and at any particular moment is opposite the same value of the optical density on the vertical axis of the graph paper as is indicated by that point along the variable disk opening which is at that moment in front of the entrance slit. The motion of the spark point along the axis of the drum is usually synchronized with the rotation of the grating and consequently with change of wave-length, but for kinetic studies the spark point is moved independently of the grating.

In order to use the instrument to full advantage in the study of reaction rates it is necessary that

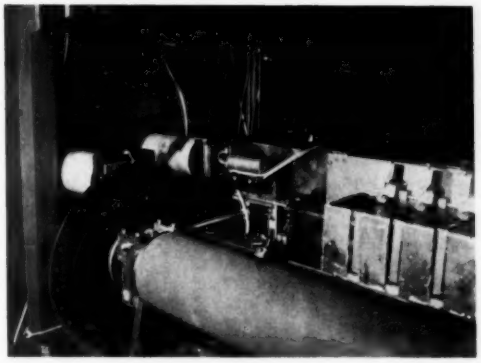

FIG. 1.

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940.

[1] G. R. Harrison, *Proceedings of the Sixth Conference on Spectroscopy* (John Wiley, New York, 1939), p. 91.

[2] G. R. Harrison and E. P. Bentley, J. Opt. Soc. Am. 30, 290 (1940).

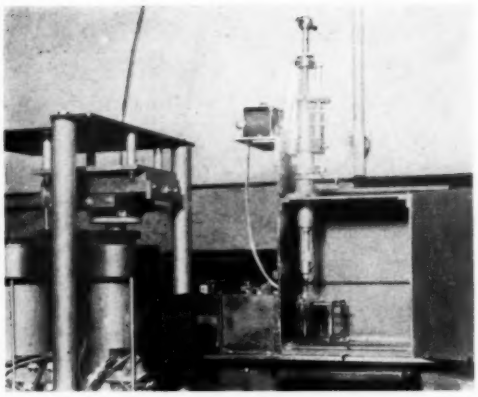

FIG. 2.

two solutions be mixed in the absorption cell in less than 0.04 second, and that this process take place during the portion of the photometric cycle in which the beam is not passing through the solution cell. The mixing device, similar to one described by Stern and Du Bois,[3] is shown in Fig. 2. It is essentially an injector, made from a hypodermic syringe the plunger of which is connected to a spring which is released automatically by a solenoid. The tip of the syringe needle is placed about 1 cm below the surface of the solution in the cell to prevent the formation of air bubbles. The mixing operation consists in the injection of a known amount of liquid from the syringe into the solution present in the absorption cell; usually about 0.5 cc of solution containing one reactant is injected into 4 cc of solution with the remaining reactants.

The solenoid is in series with a microswitch which is automatically closed momentarily at a certain point along the axis of the drum, and with a commutator rotating with the same speed as the disk which completes the circuit of the solenoid, while the microswitch is closed, during only a fraction of the cycle. By proper choice and arrangement of the commutator it is possible to prevent the injection while the beam is passing through the solution cell.

Mixing tests involving the injection of methylene blue solution into water were carried out and showed that mixing was photometrically complete within the cycle since the first density value recorded after injection was equal to subsequent values. An approximate determination of the time of mixing with the oscillograph yielded a result of about 0.02 second.

The experimental results are obtained in the form of a series of holes punched in a sheet of graph paper wrapped around the drum. A contact print of part of such a sheet with the holes enlarged is shown in Fig. 3, where the ordinate is optical density and adjacent points are separated along the abscissa by 0.05 second. The series of points at the lower left represents the constant density of the solution before mixing. After injection there is an initial rise of no significance and then a series of points recording the increasing concentration of the colored product. The series of points at the upper right represents the maximum value of optical density that can be measured by the apparatus.

APPLICATION OF TECHNIQUE

The study of respiratory enzymes has revealed a number of unique characteristics of these catalysts which have led to the suggestion that many of the reactions catalyzed by these enzymes

FIG. 3.

[3] K. G. Stern and D. Du Bois, J. Biol. Chem. **116**, 575 (1936).

proceed by way of chains involving free radicals.[4] The experimental evidence in favor of a chain mechanism is particularly strong in the case of the decomposition of hydrogen peroxide in the presence of catalase and the bioluminescent oxidation of luciferin catalyzed by luciferase.

Among the special properties of chain reactions there is the induction period which is due to the time required for the concentrations of intermediates participating in the chain to reach their maximum values and thus establish a stationary state.[5] This results in an increasing rate of formation of the products of the reaction for a short time, after which the customary decline of the rate caused by the decreasing amounts of reactants is observed. Such an effect has been found in a number of nonenzymatic reactions[5] and in one or two enzymatic reactions where the experimental arrangements have made it possible to study the course of the reaction during the first few hundredths or tenths of a second after mixing.

In order to throw some light on the mechanism of enzymatic reactions the technique described above was applied to the study of a rapid reaction catalyzed by the enzyme horseradish peroxidase with particular emphasis on the possibility of the existence of an induction period. In the presence of this enzyme hydrogen peroxide oxidizes guaiacol to a red compound known as tetraguaiacol, and it is the increasing concentration with time of this substance which was measured by the apparatus set at a wave-length of 4750A. The preliminary work carried out so far has shown definitely the existence of an induction period of the order of tenths of a second. This is indicated in Fig. 4 which illustrates the results of one experiment in which the initial concentrations in the reaction mixture were as follows: enzyme 0.101 mg per cc, hydrogen peroxide $1\times10^{-2}M$, guaiacol $1.01\times10^{-2}M$. In this case the guaiacol was injected into the solution containing hydrogen peroxide and enzyme, although in general it is preferable to inject the hydrogen peroxide. It is assumed that the concentration of the red tetraguaiacol is proportional to the optical density except for an additive factor.

The soluble enzyme preparation used was obtained from horseradish according to the method described by Keilin and Mann[6] and had an activity of P.Z.223. The experiments were carried out by injecting either a guaiacol solution into one containing hydrogen peroxide and enzyme or a hydrogen peroxide solution into enzyme and guaiacol. In both cases it was possible to observe the induction effect.

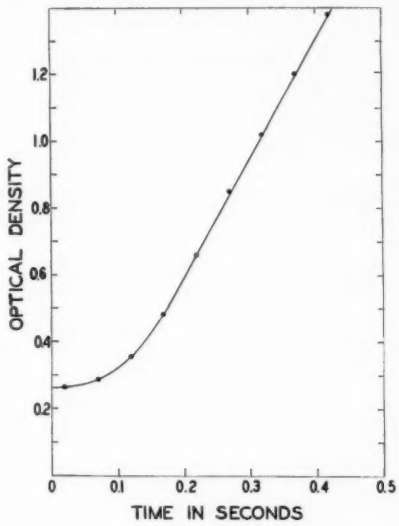

FIG. 4.

The few experimental results thus far obtained are insufficient to establish conclusively the chain nature of the reaction as the source of the induction effect. It is easily conceivable that such a result might be caused by the time required for the concentration of intermediates not engaged in a chain process to be built up especially since the formation of tetraguaiacol from guaiacol undoubtedly proceeds in a series of steps involving a number of intermediate compounds. It is also possible that the effect arises from the necessity of the enzyme to form a complex with one or both of the substrates before the reaction can start. Only the results of a quantitative study

[4] E. A. Moelwyn-Hughes, Erg. Enzymforschg. **6**, 23 (1937).

[5] N. Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford, 1935).

[6] D. Keilin and T. Mann, Proc. Roy. Soc. London **B122**, 120 (1937).

of the dependence of the induction period on the variables of the system will decide whether or not the effect serves to prove the existence of a chain mechanism in the action of horseradish peroxidase.

ACKNOWLEDGMENT

This work was carried out under a grant from the Rockefeller Foundation to Professor G. R. Harrison for the application of spectrophotometry to medical problems.

Pan-American Congress of Ophthalmology Organized at Cleveland Meeting

THE Pan-American Congress of Ophthalmology was organized on a permanent basis at the meeting of the first Congress in Cleveland, October 11–12, under the auspices of the American Academy of Ophthalmology and Otolaryngology.

Dr. Harry S. Gradle, Chicago, was elected President of the Congress. Drs. Conrad Berens, New York, and Moacyr E. Alvaro, São Paulo, Brazil, who served with Dr. Gradle as members of the committee that organized the initial meeting, were elected Executive Secretaries.

The following Vice Presidents were elected: Drs. S. Hanford McKee, Montreal, Canada; Frank E. Brawley, Chicago; Edward Jackson, Denver; Tomas R. Yanes, Havana, Cuba; A. Vasquez-Barriere, Montevideo, Uruguay; Jose Pereira Gomes, São Paulo, and Enrique Demaria, Buenos Aires, Argentina.

There will also be a council, which is to be formed by one representative from each of the twenty-one American republics. The representative from each country is to be elected by the national ophthalmological society or societies, if such exist; if there is no such society, the government of the country will be asked to appoint a member of the council.

Montevideo was tentatively selected as the place of the next meeting, to be held in 1943.

Eighteen delegates representing governments, universities, hospitals and medical societies in Brazil, Chile, Costa Rica, Cuba, Colombia, Guatemala, Panama and Puerto Rico were present in Cleveland. An extensive program of scientific papers was presented, about equally divided between English on one hand and Spanish and Portuguese on the other. English papers were discussed by Latin-American speakers; those in Spanish or Portuguese by the English speaking physicians.

The language difficulty was overcome successfully by the use of slides. Extensive summaries of the papers were projected on the slides in Spanish or Portuguese for the English ones, or in English for those given in the other languages.

Earlier in the week the Latin-American delegates were guests of the Academy at its scientific sessions and at the annual banquet, where each was formally introduced. At the Pan-American banquet held Friday night, October 11, the guests from Latin-America all expressed appreciation and enjoyment of the meeting. It was the general impression that the congress had brought about better understanding among the ophthalmologists of the Western Hemisphere. It was felt that the Latin-Americans were impressed by the meetings of ophthalmologists in this country and that the representatives of the United States were in turn impressed by the scientific ability and skill of the Latin-Americans.

At the conclusion of the meeting the Latin-Americans left to attend special clinics that were being held in their honor at some of the large ophthalmological centers of the East and Middle West.

A Spectrophotometric Study of Thionine*

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I. INTRODUCTION

THE measurement of extinction curves was formerly a tedious experimental task, followed by involved calculations. The development of automatic recording spectrophotometers has brought about a welcome change, and made the determination of the absorption spectrum nearly as simple as the measurement of the refractive index or any other physical constant. Two of these instruments—Hardy's "color analyzer" [1] and Harrison's high speed recording spectrophotometer[2]—were developed at the Massachusetts Institute of Technology, and afford a unique opportunity to obtain complete extinction curves in the range 2300–9700A. We have applied these instruments to a problem in the chemistry of dyestuffs.

The dyestuff thionine (Lauth's violet, C.I. No. 920) is of interest because of its photochemical properties. As was first discovered by Weber[3] it can use light energy to increase its oxidizing capacity to a greater extent than any compound known at present. This phenomenon is the basis of the use of thionine in photogalvanic cells[4, 5] which we are studying, and the present investigation was undertaken in connection with this research.

The dyestuff used was prepared by the National Aniline and Chemical Company, "Certified Stain" grade. While certain impurities may have been present in the dye and the solvents used, tests made on recrystallized thionine in conductivity water revealed no significant alterations in the absorption spectrum.

II. THE AGING EFFECT

Concentrated solutions of thionine deteriorate upon standing. It has been observed[6] that thionine and methylene blue (tetramethylthionine)—as well as more complex dyestuffs such as chlorophyll—are strongly adsorbed on glass surfaces. In the case of thionine, adsorption is accompanied by decomposition, causing a gradual bleaching of the solutions. Figure 1 shows the optical density of a thionine solution (initially 5×10^{-5} *m*) stored in the dark, in a glass-stoppered soft glass bottle, as a function of time. The *p*H was initially about 6, but after standing for two weeks had risen to 8.5. This suggested that the alkalinity of the glass might be a very important factor. Acid solutions of thionine (e.g., *p*H 3.5) could be stored in bottles of neutral glass (Pyrex) for months without appreciable change in absorption or in *p*H and

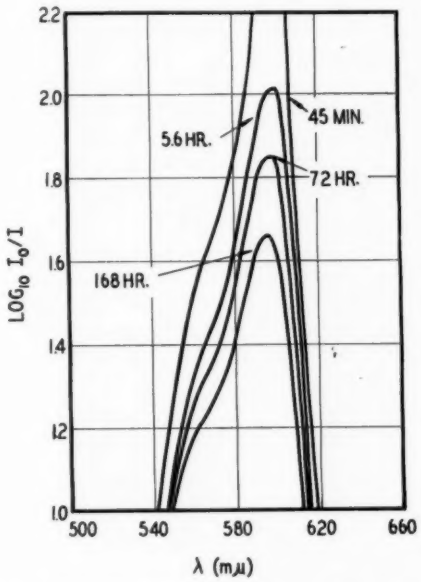


FIG. 1. Absorption spectrum of thionine solution in soft glass bottles, as function of time.

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940. Contribution No. 468, from the Research Laboratory of Physical Chemistry, and Publication No. 4, Solar Energy Conversion Research Project, Massachusetts Institute of Technology.

† Rockefeller Foundation Fellow, M.I.T. 1939–1940. Present address Johnson Foundation, University of Pennsylvania, Philadelphia, Pennsylvania.

[1] A. C. Hardy, J. Opt. Soc. Am. **25**, 305 (1935).

[2] G. R. Harrison, *Proceedings of the Sixth Spectroscopy Conference* (John Wiley, New York, 1939); G. R. Harrison and E. P. Bentley, J. Opt. Soc. Am. **30**, 290 (1940).

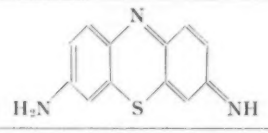
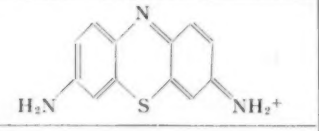
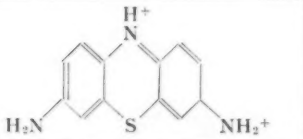
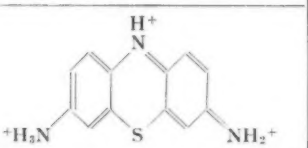
[3] K. Weber, Zeits. f. physik. Chemie **B15**, 18 (1931).

[4] E. Rabinowitch, J. Chem. Phys. **8**, 551 (1940).

[5] E. Rabinowitch, J. Chem. Phys. **8**, 560 (1940).

[6] W. M. Clark, H. D. Gibbs and B. Cohen, Public Health Reports, **40**, 1131 (1935).

TABLE I.

STRUCTURE	DESIGNATION	COLOR	STABILITY
	Thio base	Orange	Strongly alkaline solutions (5% NaOH)
	$Thio^+$	Purple	*p*H 2–10
	$ThioH^{++}$	Blue	Strong acid (up to about 5 normal HCl or H_2SO_4)
	$ThioH_2^{+++}$	Green	Very concentrated H_2SO_4 (>15 *m*)

without staining of the glass. Alkaline solutions, on the other hand were bleached upon standing even in Pyrex vessels.

The staining of glass surfaces by thionine (and methylene blue) takes place mainly above the surface of the liquid. It is therefore probable that the decomposition consists in the adsorption of the dyestuff on the glass, followed by a reaction involving atmospheric oxygen.

III. THE ABSORPTION SPECTRUM AS A FUNCTION OF *p*H [7]

Thionine contains three basic nitrogen atoms: one in the quinone-imino group, one primary amino nitrogen, and one ring (tertiary) atom.[8] Therefore this molecule should exist in at least three ionic forms in addition to the free base [7(b)] (cf. Table I). Further, the thionine molecule is capable of taking on an electron and thus being reduced to a semiquinone[9] ("semithionine") and a second electron thus forming the leuco-base ("leucothionine"). The complete scheme is shown in Table II.

TABLE II.*

← ADDITION OF PROTONS	ADDITION OF ELECTRONS →		
	THIONINE	SEMITHIONINE	LEUCOTHIONINE
	Thio base		
	$Thio^+$	Thio	$Thio^-$
	$ThioH^{++}$	$ThioH^+$	ThioH
	$ThioH_2^{+++}$	$ThioH_2^{++}$	$ThioH_2^+$
		$ThioH_3^{+++}$	$ThioH_3^{++}$
			$ThioH_4^{+++}$

* The designations used in this chart follow from those defined in Table I.

[7] Earlier papers on thionine and its spectrum are: (*a*) J. H. Stebbins, Jr., J. Am. Chem. Soc. **6**, 304 (1884); (*b*) A. Bernthsen, Ann. **230**, 111, 209 (1885); (*c*) M. Althausse, and G. Kruss, Ber. **22**, 2066 (1889); (*d*) Formanék and E. Grandmougin, *Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege* (Berlin, 1908), Part 1, pp. 143, 150; (Berlin, 1911), Part 2, p. 124. (*e*) F. Eckert and R. Pummerer, Zeits. f. physik. Chemie **87**, 613 (1914); (*f*) F. Eckert, R. Pummerer and S. Gassner, Ber. **47**, 1495 (1914); (*g*) F. Kehrman, E. Havas and E. Grandmougin, Ber. **46**, 2131 (1913); **47**, 1881 (1914); (*h*) F. Kehrman, Ber. **49**, 1018 (1916); (*i*) F. Kehrman and P. Zybs, Ber. **52**, 130 (1919); (*j*) L. Michaelis, M. P. Schubert and S. Granick, J. Am. Chem. Soc. **62**, 204, 1802 (1940).

[8] The possibility of an orthoquinoid structure, with the heterocyclic sulfur forming a sulfonium base (as was hypothesized in the older literature[7]) cannot be entirely dismissed, although the evidence seems to be against it.[7(i)]

[9] L. Michaelis and M. P. Schubert, Chem. Rev. **22**, 437 (1938).

In the formulas for $Thio^+$ and $ThioH^{++}$ in Table I the molecules appear unsymmetrical. However, these formulas represent only one of two resonating structures; in the second one, the other of the two benzene rings is in the quinoid form, and as a result of the resonance between these two structures, the molecules are perfectly symmetrical. This resonance lends stability to the molecule,[10] and the oscillating electron may be considered the principal source of the chromogenic properties.[11]

We have followed Michaelis[7i] in assigning the second proton to the bridge nitrogen, since the $ThioH^{++}$ ions are strongly colored. Introducing the proton into the amino group (as we might be tempted to do on the basis of classical organic chemistry where primary amino nitrogen is usually considered more basic than tertiary nitrogen) would destroy the possibility of resonance and therefore tend to decrease the intensity of absorption. In confirmation of these concepts, the trivalent ion $ThioH_2^{+++}$ has less than half the absorption of the other two species (cf. Fig. 6); they are further supported by purely chemical evidence.[7i]

In the figures which follow, the spectra of seven out of the thirteen species listed in Table II are given. The curves are expressed either in terms of the optical density ($\log_{10} I_0/I$), or the molecular extinction coefficient

$$\epsilon = (1/dc) \log_{10} I_0/I$$

where d is the cell thickness in centimeters and c is the concentration in moles per liter. It has been reported that many dyestuffs do not obey Beer's law[12] although the accuracy of the photometric measurements is often questionable. Using cells about 0.01, 0.1, 1, and 10 cm thick, we have studied the effect of concentration on the spectra of thionine and methylene blue over the range 2.5×10^{-3} to 2.5×10^{-7} mole per liter.

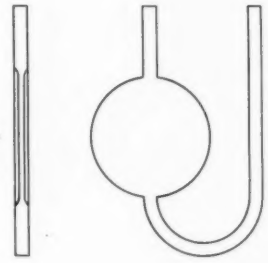


FIG. 2. Thin cells.

EXPERIMENTAL

The exact dimensions of the cells used were

0.01	0.00832 cm
0.1	0.1053
1.	1.0097
10.	9.9971.

The two larger cells were commercial, made of glass. The thin cells were made from two round optically flat quartz plates, worked into the shape shown in Fig. 2.[13] The cells were calibrated by measuring the absorption of each of our thionine solutions in *two* cells. The thickness of the one-centimeter cell could be accurately determined with a micrometer, and the dimensions of the other cells calculated from this by the equation $d_1\times[\log_{10}(I_0/I)]_2 = d_2\times[\log_{10}(I_0/I)]_1$. Matched one-centimeter cells were used for the solvent and the solution; with the other cells, it was necessary to determine two curves one for the solution and a second for the pure solvent. All the measurements with the Hardy machine were made in a laboratory thermostated at 80°F (26.7°C).

For the Harrison spectrophotometer, only one-centimeter quartz cells (accurate to better than 0.1 percent) were available, so that concentration effects could not be studied in the

[10] L. Pauling and co-workers, J. Chem. Phys. **1**, 362, 606, 679 (1933); cf. also *The Nature of the Chemical Bond*, 2nd edition (Cornell University Press, Ithaca, New York, 1940).

[11] C. R. Bury, J. Am. Chem. Soc. **57**, 2115 (1935); A. L. Sklar, J. Chem. Phys. **5**, 669 (1937); L. Pauling, in H. Gilman, *Organic Chemistry* (John Wiley, 1938), II, p. 1888; L. Pauling, Proc. Nat. Acad. Sci. **25**, 577 (1939); G. N. Lewis and M. Calvin, Chem. Rev. **25**, 273 (1939); R. S. Mulliken, J. Chem. Phys. **7**, 14, 20, 121, 339, 353, 356, 364, 570 (1939).

[12] (*a*) W. C. Holmes, Ind. Eng. Chem. **16**, 35 (1924), Am. Dyestuff Rep. **16**, 429 (1927), J. Am. Chem. Soc. **50**, 1923 (1928); (*b*) G. Körtum, Zeits. f. physik. Chemie **B30**, 317 (1935), **31**, 137 (1935), **31**, 1, 243 (1936), **34**, 255 (1936); (*c*) W. E. Speas, Phys. Rev. **31**, 539 (1928); (*d*) G. Scheibe, Kolloid, Zeits. **82**, 1 (1938); G. Scheibe and L. Kandler, Naturwiss. **26**, 412 (1938); G. Scheibe, A. Schöntag, J. Kopske and K. Meule, Zeits. f. wiss. Phot. **38**, 1 (1939); G. Scheibe, A. Schöntag and E. Katheder, Naturwiss. **27**, 499 (1939); (*e*) V. L. Lewshin, Acta Physicochimica, U. R. S. S. **1**, 685 (1935), **4**, 221 (1936).

[13] Made by Mr. Henry Wayringer, to whom we wish to express our thanks.

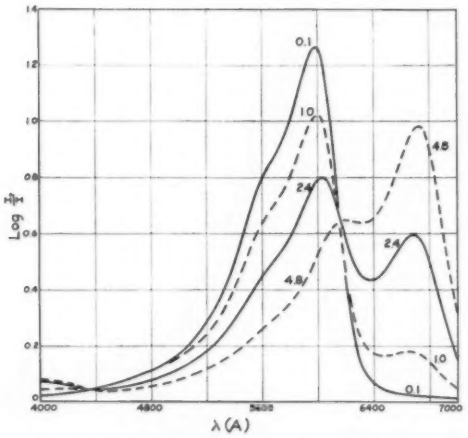


FIG. 3. The spectrum of thionine (2.5×10^{-5} *m*) in HCl solution (acid concentrations in moles/l).

ultraviolet region. Here all measurements were made at 25°C.

In the *p*H range 2–10, the purple thionine solutions ($Thio^+$) show large deviations from Beer's law—a variation in the relative heights of two bands, one (597 mμ) decreasing in height as the solution becomes more concentrated while a second band (557 mμ) grows stronger. This phenomenon is caused by the dimerization of the dyestuff; calculations and detailed evidence for this hypothesis will be presented elsewhere.[14]

The transition from the monovalent ion $Thio^+$ to the divalent ion $ThioH^{++}$ on decreasing the *p*H is illustrated by Fig. 3, where the spectrum of thionine (2.5×10^{-5} *m*) in HCl solutions is shown as a function of acid strength. In tenth molal acid, the spectrum is still that of $Thio^+$; but as the acid concentration increases, the 597 mμ band of the monovalent ion decreases and simultaneously a band characteristic of the divalent species appears at 673 mμ. The color gradually changes from purple to blue. The curves all cross at a single point (614 mμ). At this wave-length the $Thio^+$ and $ThioH^{++}$ bands must have equal intensities. The occurrence of a single "isobestic" point[15] indicates that we are dealing with a mixture of only *two* absorbing species.

From the change in the absorption spectrum with acid strength, we should be able to calculate the dissociation constant of the divalent thionine ion

$$ThioH^{++} \rightleftharpoons Thio^+ + H^+$$
$$K_1 = (Thio^+)(H^+)/(ThioH^{++}).$$

We find $K_1 = 47.3$; however, the exact meaning of the dissociation constant in solution of such high acidity is doubtful.

The transition from the purple to the blue form can also be observed in H_2SO_4 solution. In sulfuric acid hydrogen ion concentrations considerably greater than in concentrated HCl can be obtained, and we may thus also observe the transition.

$$ThioH^{++} + H^+ \rightleftharpoons ThioH_2^{+++}$$

from the blue divalent to the pale-green trivalent form. In Fig. 4 (2.5×10^{-5} *m* in thionine) the least acid solution, 9.4 *m* in H_2SO_4, has an absorption spectrum similar to that of the most concentrated HCl solution in Fig. 3. But as the acid strength goes up, the concentration of the trivalent ion increases and the spectrum again changes in a characteristic way. The long wave-length band in concentrated H_2SO_4 is broader, flatter, and lower than in strong HCl; a maximum seems to occur at $\lambda \cong 640$ mμ. This band, however, is probably made up of two peaks (evident in the original spectrophotometer record) with

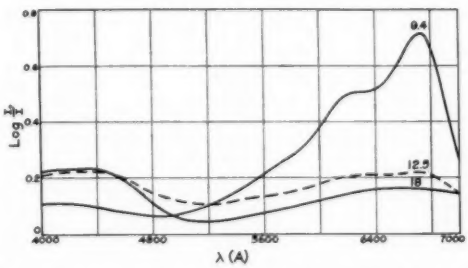


FIG. 4. The spectrum of thionine (2.5×10^{-5} *m*) in strong H_2SO_4 solution (acid concentrations in moles/l).

[14] E. Rabinowitch and L. F. Epstein, "The polymerization of dye-stuffs in solution. Thionine and methylene blue." Presented at the Symposium on Structure of Molecules and Aggregates of Molecules, Division of Physical and Inorganic Chemistry, American Chemical Society, Columbia University, New York, New York, December 30, 1940 to January 1, 1941. J. Am. Chem. Soc., paper in press.

[15] A. Thiel, A. Dassler and F. Wülfken, Fortschritte Chemie, Physik, u. physik. Chemie **18**, 4.3 (1924); E. B. R. Prideaux, Chem. Industry, **45**, 664, 678 (1936); cf. W. M. Clark, *Determination of Hydrogen Ions* (Baltimore, 1928), p. 206.

equal maxima at about $\lambda = 630$ mμ and 675 mμ, and a very shallow minimum at 652 mμ. There is a second band, also broad and weak, at the extreme end of the visible spectrum, $\lambda = 425$ mμ. This second band can also be seen in solutions of $ThioH^{++}$ and in solutions of $Thio^{+}$ containing high concentrations of neutral salt;[16] it seems likely that it is caused by undissociated complexes of the cation with the anion. Because of this and other complications, we did not attempt to calculate the acid dissociation constant of $ThioH_2^{+++}$, as was done above for $ThioH^{++}$.

Adams and Rosenstein[17] in a spectrophotometric study of the dyestuff crystal violet found changes with acid concentration quite similar to those reported here—two strongly colored ionic forms, and a third one only slightly colored.

At the extreme alkaline end of the *p*H scale, we observe changes caused by the formation of the free thionine base and non-ionized thionine hydroxide:

$$R{=}NH_2^{+} + OH^{-} \rightleftarrows R{=}NH_2OH \rightleftarrows R{=}NH + H_2O \quad (1)$$

$$Thio^{+} \rightleftarrows \text{Thio hydroxide} \rightleftarrows \text{Thio base.}$$

The free base is less soluble than the salts, and a white precipitate comes down in concentrated $Thio^{+}$ upon the addition of alkali. In solution, the free base is red-orange. As the OH^{-} ion concentration decreases and we pass from this form (the 5 percent NaOH curve in Fig. 5) to the purple $Thio^{+}$ solutions, a whole range of red colors is obtained. The occurrence of the two species RNH_2OH and $R{=}NH$ probably accounts for the fact that the curves in Fig. 5 do not all pass through a single point (cf. Fig. 3), and makes it difficult to determine the mass action constants of the reactions (1). From the e.m.f. data of Clark[6] the transition from Thio OH to $Thio^{+}$ occurs at about *p*H 11, which is consistent with our optical data. (It may be pointed out that methylene blue can form only the hydroxide but not the free base, since this would necessitate the splitting out of methanol. This difference may be responsible for the fact that there is no kink in the $E_0' = f(p\text{H})$ curve of this compound in the alkaline region).[6]

[16] Cf. reference 14, Fig. 3.

[17] E. Q. Adams and L. Rosenstein, J. Am. Chem. Soc. **36**, 1452 (1914).

In this discussion, we have omitted certain complications that arise through irreversible reactions. In strong HCl (8 molal or over), the blue-green thionine solutions lose their color upon standing. This effect is considerably reduced, but not entirely eliminated in H_2SO_4 solution. The bleaching does not seem to involve the oxidation of HCl to free Cl, and the nature of the reaction remains unknown.[18] Red-orange alkaline solutions of Thio base also become completely colorless upon standing.[19] This reaction is probably the cause of the bleaching of thionine solutions in glass vessels (cf. Section II).

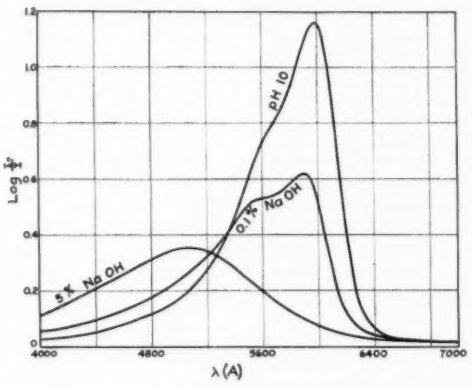


FIG. 5. The spectrum of thionine (2.5×10^{-5} *m*) in alkaline solution.

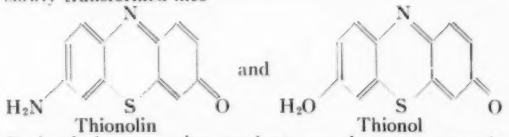
It seems that only the monomeric ions $Thio^{+}$ dimerize in solution. Presumably the increased electrostatic repulsion between polyvalent ions tends to stabilize the monomeric forms.

IV. The Ultraviolet Spectrum of Thionine

Figure 6 shows the extinction curves of thionine over the range $\lambda = 230$–970 mμ, determined

[18] Adams and Rosenstein (cf. reference 17) also observed irreversible bleaching in acid solution of crystal violet, and studied the kinetics of the bleaching process. In this case the bleaching in acid solutions seemed to be independent of the anion.

[19] Beilstein reports that alkaline solutions of thionine are slowly transformed into



Thionolin Thionol

Both of these reaction products are, however, strongly colored.

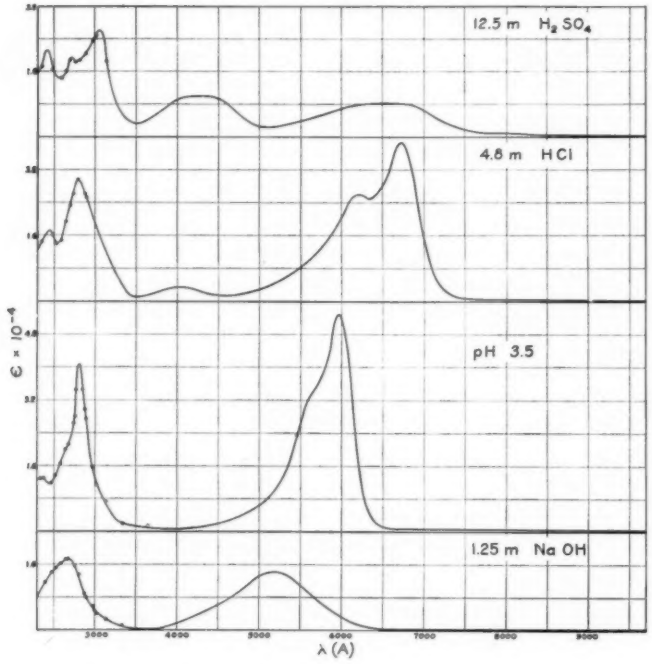


FIG. 6. Extinction curves of thionine solutions (2.5×10^{-5} *m*).

with the Harrison spectrophotometer. All curves were made at 2.5×10^{-5} *m* in one-cm cells. From 350 mμ out into the infra-red, a tungsten lamp operated at 180 volts was used to obtain continuous readings; at the shorter wave-lengths, the spectrum was obtained semi-automatically using lines in the spectrum from a high pressure mercury arc.

In the visible region, the agreement with the Hardy curves is excellent. No new bands appear in the infra-red. The bands near 400 mμ, may, as we have previously said, be caused by undissociated complexes with the anions. All of the ionic species of thionine have absorption bands in the ultraviolet, which are, however, considerably weaker than the visible bands, except in the case of the weak dye $ThioH_2^{+++}$. In addition to the main rather intense band between 250 and 320 mμ for the various species, there is a secondary peak which just shows up in the spectrum of the monovalent form $Thio^+$ and increases in intensity as we pass to the acid species $ThioH^{++}$ and $ThioH_2^{+++}$. Table III lists the principal absorption bands of thionine.

For purposes of comparison, the absorption spectrum of methylene blue (in the monovalent form MB^+) is given in Fig. 7.

V. THE SPECTRA OF LEUCOTHIONINE AND SEMITHIONINE

Leucothionine was prepared by the reduction of the dyestuff (in solutions buffered with KH_2PO_4, Na_2HPO_4, and HCl—all molecules which do not absorb light above 230 mμ) with finely divided palladium[20] and hydrogen at *p*H's which, according to the electrochemical data[6] should correspond to the three ionic forms ThioH, $ThioH_2^+$, and $ThioH_3^{++}$. There is a peak at

TABLE III. *Principal absorption maxima (mμ) of thionine* (2.5×10^{-5} *m*).

SPECIES	λ	ε×10⁻⁴	λ	ε×10⁻⁴	λ	ε×10⁻⁴	λ	ε×10⁻⁴
Thio base	515	1.42	—	—	268	1.67	—	—
$Thio^+$	597	5.52	—	—	281	4.06	—	—
$ThioH^{++}$	673	3.87	405	0.34	279	2.96	245	1.72
$ThioH_2^{+++}$	630 675	0.80	430	0.98	304	2.62	241	2.12

[20] We are indebted to Professor L. J. Gillespie and Dr. S. D. Stookey of this laboratory for the special Pd used in these experiments.

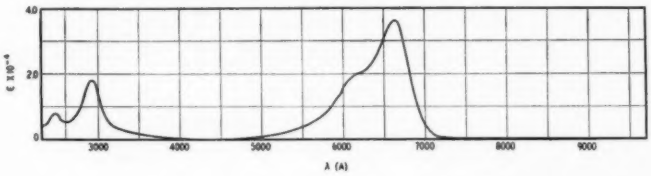


FIG. 7. Extinction curve of methylene blue (2.0×10^{-5} *m*, *p*H 3.5).

about 250 mμ for all three species (Fig. 8) of about the same height as the corresponding thionine maxima. In addition to this main band there is evidence of another maxima at $\lambda<230$ mμ which appears to be more prominent in the alkaline solutions. (Cf. absorption at 230 mμ of the three species in Fig. 8.) It was not possible to obtain the spectrum of the leuco-ion Thio$^-$ since in alkaline solutions, where it should be stable, the reduction with H_2 and Pd is too slow.

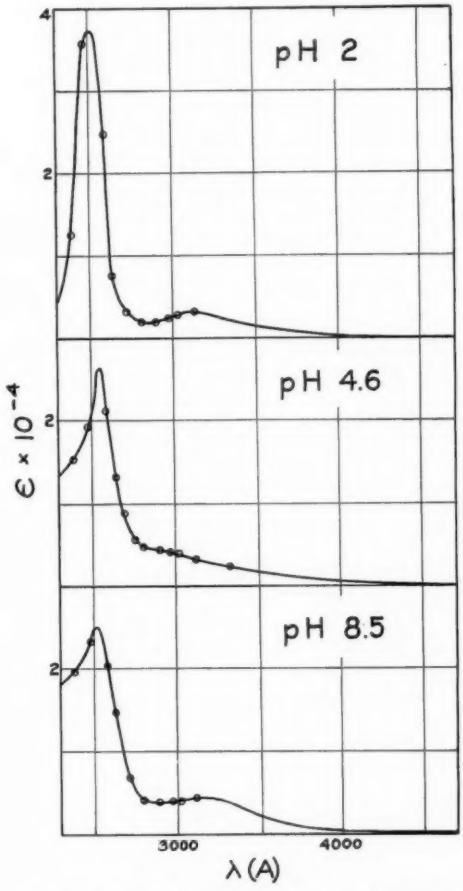


FIG. 8. Ultraviolet absorption spectra of leucothionine.

Differences between the ultraviolet absorption spectra of the three ionic species of leucothionine are of a minor character, as are those of the ultraviolet spectra of the thionine ions, compared with the strong effects which the association with protons has on the visible absorption bands of the dye.

We also attempted to identify the bands of semithionine, but obtained no positive results. The spectrum of semithionine in 15 *m* H_2SO_4 was described by Michaelis and co-workers;[7i] it consists of several bands in the region 438–512 mμ, with maxima of the order of $\epsilon=0.7\times10^4$. This indicates a very weakly colored orange-yellow form. It must be one of the ionic species ThioH$^+$ or ThioH$_2^{++}$ (cf. Table II). These species are comparatively stable (Michaelis) with respect to dismutation

$$2\ \text{Semithionine} \rightleftharpoons \text{Thionine} + \text{Leucothionine}$$

because they are capable of a resonance similar to that mentioned above as stabilizing the ions Thio$^+$ and ThioH^{++}. In less acid solutions, semithionine must be present in the neutral form Thio which, because of the absence of resonance is probably both unstable and colorless. According to Michaelis[7i] the concentration of semithionine in a half-reduced solution for $p\text{H}>1$ is about 5–10 percent. We have searched for the absorption bands of semithionine in this region by analyzing the extinction curves of mixtures of equal parts of thionine and leucothionine in terms of the extinction curves of the pure species. No indications of semithionine bands were found in the visible region. This indicates that if such bands do exist at all, their intensity must be much less than that of the Thio$^+$ band, so that 5–10 percent of semithionine cannot be detected spectrophotometrically. In the ultraviolet region, the use of discontinuous light source made the resolution insufficient for a successful search for the semithionine bands.

We wish to thank Professor A. C. Hardy and Dr. S. Q. Duntley of the M.I.T. Color Measurements Laboratory for their friendly cooperation in this work.

Summary

(1) Solutions of thionine are strongly adsorbed on soft glass and irreversibly decomposed. Decomposition can be prevented by the use of Pyrex vessels and moderately acid solutions. Alkaline solutions (containing the free thionine base) as well as solutions in strong HCl are bleached upon standing, even in Pyrex vessels.

(2) The absorption spectra of four forms of thionine and three forms of leucothionine have been investigated over the range 230–970 mμ as a function of concentration. An attempt to identify the bands of semithionine in moderately acid solution was unsuccessful.

(3) Thionine follows Beer's law (except for effects caused by the presence of other ions) in solutions containing the free base, and trivalent ions. Solutions of the monovalent ion $Thio^+$ (*p*H 2–10) on the other hand, show large deviations even at concentrations as low as 10^{-6} mole per liter, because of dimerization.

Note on a Spectrographic Study of Central American and Asiatic Jades*

DANIEL NORMAN AND W. W. A. JOHNSON
New England Spectrochemical Laboratories, Boston, Massachusetts

VERY few of the numerous Maya jade objects now in museums have ever been chemically analyzed. The largest compilation of analyses was published by Washington[1] of the Carnegie Institution in 1922. It contained only thirteen analyses, four of which had been previously published. The matter is of considerable archaeological interest because the sources of these Central American jades are still obscure—a fact which has given rise to the suggestion that they may have been imported from the Orient, and therefore that the Mayas had been in contact with, and were influenced by, the culture of the Orient.

Washington showed that, while the American jades belonged to the general group of jadeite jades, they differ from the usual jadeite of Burma and China by the constant presence of considerable amounts of diopside. Seven of the thirteen jades analyzed by Washington were from the collection found by Tozzer of Harvard University in a sacred natural well at the ancient Maya city of Chichen Itza in northern Yucatan. Professor Tozzer has very kindly lent us twenty-four jade disks and beads found in the sacred well, including seven previously analyzed by Washington. Professor Berman, also of Harvard University, very kindly gave us samples of seven jades of known provenance—four from China, one from Burma, one from New Zealand, and one from New York.

A sufficiently large sample of each jade was analyzed to yield a representative analysis. Too large a sample could not be used because jade proved to be a very superior insulator. The average size of the sample analyzed was four-tenths of a cubic centimeter, and difficulty was found in burning even this size sample in a ten-ampere carbon arc. The jade was so hard that it was not found practical to shape or pulverize the samples. All we could do was to break off a sample of about the right size from the original jade ornament. All the samples were arced at ten amperes in a cored carbon electrode focused on the slits of the spectrographs. The spectra were photographed with two grating spectrographs—the wave-length range from 2200A to 3300A was photographed with a three-meter Baird Associates spectrograph (Wood aluminum-on-glass concentrating grating) while the range from 3300A to 6800A was photographed on a one-meter Cenco spectrograph.

The results of the spectrographic analyses are given in Table I. The first column contains the museum designation of the jade samples; the remaining columns list the estimated amount of each element present on the arbitrary scale of: (1) greater than 4 percent, (2) 4 percent to 0.2 percent, (3) 0.2 percent to 0.01 percent, (4) less than 0.01 percent. A colon after the amount indicates that the estimated order of magnitude is uncertain.

In general, these analyses are in agreement with those published by Washington. Unfortunately he did not publish the museum numbers of the samples he analyzed, so it is not possible to compare the analyses of the seven samples which were common to both lists. No phosphorous was found in any of the American jades, although it is often found in Asiatic jades. The resemblance between jades *E*, *W*, and H.U. 31472 (a nephrite from China) is striking. The nominal formula for jadeite is $NaAl(SiO_3)_2$, which fits well with the amount of aluminum spectrographically observed, but the low aluminum content of these three samples suggests that they are primarily diopside (nominally $CaMgSi_2O_6$), a mineral commonly found in solution in American jadeite. Washington found one jade—the Tuxtla statuette,[2] the oldest dated Central American object—which was over 50 percent diopside, and was characterized by the absence of chemically detectable amounts of

* Presented at the Eighth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, July, 1940.

[1] H. S. Washington, Proc. Nat. Acad. Sci. **8**, 319 (1922).

[2] H. S. Washington, Proc. U. S. Nat. Museum **60**, 1 (1922).

TABLE I. *Analyses of jades.**

DESIG.	Ag	Al	B	Ba	Be	Ca	Cd	Cr	Cu	Fe	K	Li	Mg	Na	Ni	Pb	Rb	Si	Sn	Ti	V	Zn
A	4	1		4		1		4	4	2	4	3	1	1	4		3	1	3	2	4	1
B		1	3		4	3		4	4	2	4:		1	1	4	4	4	1	4	4	4	1
B'		1	3		4	3		4	4	2	4:	3	1	1	4		4	1		4		1
C	4:	1	4	2		2		4	4	1	4	3	2	1	3	2	3	1	4	4		1
D		1	3	4		2		4	4	2	4	2	1	1	4	4	3	1		3	4	1
E		4	4	4	4	2		2	4	2	4:		1	1	2	4	2	1			4	4
F	4	1		3		1		4	5	2	4	3	1	1			4	1		4	4	1
G		1	4	2		1		4	4	1	4	3	2	1	3	4	3	1	4	2	4	1
G'	4	1	4	2		2		4		1	3	2	1	1	2	4	3	1	4	4	4	1
H	4	1	4	4		1		4	4	1	4	3	1	1	4		3	1		3	4	1
H2	4	1	4	3		2			4	2	4	2	1	1	4	4	3	1		3	4	1
J		1	4			2		4	4	2	4	2	1	1	4	4	4	1	4			1
K		1		4	3	1		3		2	3	3	1	1	4		3	1	4		3	1
L		1				1		4	4	2		3	1	1	3		4	1	4	4	4	1
N	4:	1	4			2		4	4	1	4	4	2	1	4	4	3	1		4	4	1
O		1	4			2				1		2	1	1	4		4	1			4	1
P		1	3	3	4	1		3	4	2	3	2	1	1	2		3	1	4	3	3	1
Q	4	1		3		1		4	4	2	4	3	1	1	3		4	1	4	3	4	1
R	4	1	4	3		1	4	4	3	1	4	3	2	1	4	4	3	1	2	2	3	1
S	2	1		4		1		4	3	1	4	3	3	1	3	4	4	1	2	4	4	1
T	4	1	4			4			3	2		3	3	3		4:		1	4		3	1
U		2	4	3		2		4		1	4		1	1	4		3	1	3	2	3	2
V	4	1		3		1		4	4	1	3	3	2	1	4		3	1	3	2	3	3
W	4	3	4	4		2		4	3	1	2	4	1	4	3	3	3	1	2		4	
H.U. 31472[a]	4	4	2			2		4	3	4	4		2	4		4	3	1	4		4	
H.U. 85254[b]	3	1	4	4		2		4	3	1	4	4	1	1	3	4	4	1	2	4	4	2
H.U. 37503[a]	4	2				4		4	4	2	4	4	2	1	4	4	4	1	4			1
H.U. 88401[a]	4	1	4	4		1		2	4	1	4	4	1	1	3	4	3	1	4	2	4	1
H.U. 88402[c]	4	2	4	4		1		2	3	1	4		1	4	2		2	1	3		4	4
H.U. 88403[a]	3	1		2		2		4	3	1	4	4	1	1	4		3	1	3	4		2
H.U. 94343	4	1	4	4		2		3	1	4	3	2	1	3	4	3	1	4	3	4	3	1
H.U. 94838[d]	4	3	4	3		1		3	4	1	4	1	1	1	4	4	2	1	4	2	3	4

* (a) Jades from China; (b) Burma; (c) New Zealand; (d) DeKalb, New York.
All other Jades are from Chichen Itza.

titanium and chromium, both present only as spectrographic traces in samples *E*, *W*, and H.U. 31472.

A comparison of the spectrographic data with the large number of careful analyses of oriental jades published in Bishop's jade book[3] shows that there is no marked chemical difference between the jades of America and those of the orient—the differences are wholly mineralogical.

[3] H. R. Bishop, *Investigations and Studies in Jades* (Privately printed, 1906).

Proposed American Standard: Specifications for Determining Photographic Speeds of Roll Films, Film Packs and Miniature Camera Films*

AMERICAN STANDARDS ASSOCIATION
COMMITTEE ON STANDARDIZATION IN THE FIELD OF PHOTOGRAPHY
SUBCOMMITTEE ON SENSITIVITY TO RADIANT ENERGY

FOREWORD

THESE proposed American Standard Specifications for Determining Photographic Speeds of Roll Films, Film Packs, and Miniature Camera Films are designed to provide an accurate and reproducible method of determining and expressing the photographic speed of individual samples of the types of negative materials covered. Additional standards, specifications, and methods for determining the speed of other classes of sensitized photographic materials are being developed. The speed criterion upon which these proposed standards are based was first suggested by experimental work reported in various technical journals.** The British Standards Institution first proposed the technique for development used herein and their procedure is included with the consent of that Institution.

The subcommittee is still working on some of the individual features of these proposals for determining speed, but such progress has been made toward unanimous agreement that the subcommittee recommends publication of the proposals in their present form for wider examination and comment. After a period of approximately one year, the specifications will be reconsidered by the subcommittee, revised if necessary, and submitted to the American Standards Association for approval as an American Standard.

The use of the initials ASA, the words American Standard, or any similar designation, in connection with film speed numbers determined in accordance with these proposed specifications, is prohibited during the trial period pending adoption of the method.

The American Standards Association as a member of the International Standards Association is the secretariat of the ISA project on Photography, ISA 42. These specifications are being circulated for comments to those countries holding membership on ISA Committee 42 and also to the International Congress of Scientific and Applied Photography which also participates.

Suggestions for improvement based upon experience gained in the use of these proposed specifications will be welcomed for the guidance of the committee. Suggestions should be sent to the American Standards Association, 29 West 39 Street, New York, New York as soon as possible and not later than January 1, 1942.

The ASA Committee on Standardization in the Field of Photography was initiated in September, 1938, on the recommendation of a general conference of the American photographic industry following a request from the International Standards Association that the ASA accept the secretariat for ISA Committee 42 on Photography. The Optical Society of America was designated as sponsor for the ASA project.

The scope for the ASA project is as follows:

"The formulation of definitions, dimensional standards, and recommended practices in the field of photography, and the establishment of methods for testing, rating, and classifying the performance characteristics of materials and devices used in photography, including its industrial applications, but excluding cinematography."

* Not approved: published for trial and criticism. The Optical Society of America is sponsor for the project.

** "The Evaluation of Negative Film Speeds in Terms of Print Quality," Loyd A. Jones, J. Frank. Inst. **227**, 297 and 497 (1939). "A Study of Various Sensitometric Criteria of Negative Film Speeds," Loyd A. Jones and C. N. Nelson, J. Opt. Soc. **30**, 93 (1940).

The membership of the ASA Committee on Standardization in the Field of Photography, Z38, is as follows:

LOYD A. JONES, *Chairman*
J. W. MCNAIR, *Secretary*

Organization Represented	*Name of Representative*
Optical Society of America (Sponsor)	C.W. GARTLEIN A.C. HARDY LOYD A. JONES BRIAN O'BRIEN
Agfa Ansco—A Division of General Aniline & Film Corporation	PAUL ARNOLD JOHN FORREST
American Astronomical Society	FRED L. WHIPPLE
American Chemical Society	S.E. SHEPPARD
American Committee of the International Congress of Photography	WALTER CLARK
American Microscopical Society	OSCAR W. RICHARDS
American Geophysical Union	CAPT. T.J. MAHER
American Optical Company	E.D. TILLYER O.W. RICHARDS (*Alt*)*
American Roentgen Ray Society	FRED O. COE, M.D.
American Society of Photogrammetry	O.M. MILLER
American Society for Testing Materials	L.V. FOSTER H.E. SEEMANN (*Alt*)
Bausch & Lomb Optical Company	W.B. RAYTON L.V. FOSTER (*Alt*)
Biological Photographic Association	LOUIS SCHMIDT RALPH P. CREER (*Alt*)
Cambridge Instrument Company, Inc.	U.O. HUTTON
Defender Photo Supply Company, Inc.	ROWLAND S. POTTER A.D. JACKLING (*Alt*)
DuPont Film Manufacturing Corporation	V.B. SEASE D.R. WHITE (*Alt*)
Eastman Kodak Company	M.E. RUSSELL W.S. VAUGHN WALTER CLARK (*Alt*) F.M. BISHOP (*Alt*)
Electrical Testing Laboratories	S.MCK. GRAY J.H. LEICHT (*Alt*)
Fairchild Aerial Camera Corporation	GEORGE RATTRAY IRVING DOYLE (*Alt*)
Folmer Graflex Corporation	GAYLORD C. WHITAKER CHARLES H. ROTH (*Alt*)
The Gevaert Company of America, Inc.	JOSEPH H. COENEN
The Haloid Company	HANS DESSAUER
The Interchemical Corporation	CARL E. FOSS F.L. WURZBURG, JR (*Alt*)
International Research Corporation	GUSTAVE FASSIN
E. Leitz, Inc.	AUGUSTUS WOLFMAN
Lithographic Technical Foundation, Inc.	PAUL W. DORST
Master Photo Finishers of America	ALBERT F. HOGLE
National Electrical Manufacturers' Association	J.S. COWLES W.N. GOODWIN, JR. F.K. MCCUNE
The National Photographic Dealers' Association	H.O. BODINE
The Photo Finishing Institute	ALBERT F. HOGLE JOSEPH G. TAYLOR (*Alt*)
Photo Utilities, Inc.	JOSEPH M. BING C.W. GIBBS (*Alt*)
The Photographers' Association of America	WILLIAM GERDES
Photographic Society of America	JOHN R. WEBER
Radiological Society of North America	D.S. CHILDS, M.D.
Society of Motion Picture Engineers	J.I. CRABTREE
U.S. Department of Commerce, Coastal Geodetic Survey	COMDR. O.S. READING CAPT. T.J. MAHER (*Alt*)
U.S. Department of Commerce, National Bureau of Standards	RAYMOND DAVIS
U.S. Navy Department	LT. R.S. QUACKENBUSH, JR.
U.S. War Department—Air Corps	GEORGE MAGNUS
U.S. War Department—Signal Corps	ROBERT F. NICHOLSON
Carl Zeiss, Inc.	V.E. WHITMAN
Universal Camera Corporation	P.H. CASE GEORGE KENDE (*Alt*)

* *Alt*—abbreviation for alternate.

Nine subcommittees have been appointed to develop standards, specifications, and methods of test under the above broad scope which covers the whole photographic field. The assignments of the subcommittees are as follows:

Subcommittee 1—Physical dimensions of sensitive materials, specifically of unexposed, unprocessed, sensitive materials and holders therefor.
Subcommittee 2—Sensitivity to radiant energy.
Subcommittee 3—Supports for sensitive coatings.
Subcommittee 4—Exposing equipment: cameras, lenses, shutters, etc.
Subcommittee 5—Photographic characteristics of illuminants.
Subcommittee 6—Processing equipment.
Subcommittee 7—Printing and projection equipment.
Subcommittee 8—Processing.
Subcommittee 9—Definitions; abbreviations and symbols; form and arrangement of published standards; numbering of standards.

The Subcommittee on Sensitivity to Radiant Energy, Subcommittee No. 2, which developed the proposed specifications included herewith, has the following personnel:

M. E. RUSSELL, *Chairman*

PAUL ARNOLD
WALTER CLARK
RAYMOND DAVIS
W. N. GOODWIN, JR
S. MCK. GRAY
ALBERT F. HOGLE
F. K. MCCUNE
BRIAN O'BRIEN
ROWLAND S. POTTER
E. D. TILLYER
D. R. WHITE
HANS DESSAUER

1. SENSITOMETRIC CRITERION OF SPEED

1.1 SPEED shall be computed by the use of the formula:

$$\text{Speed} = 1/E,$$

where E is the exposure (expressed in meter-candle-seconds) corresponding to the point on the density-$\log_{10}$ exposure curve at which the gradient is 0.3 times the average gradient for a $\log_{10}$ exposure range of 1.50 of which E is the minimum exposure.

1.2 SPEED NUMBERS determined by the above formula are not suitable for, nor intended for, use with exposure meters or exposure calculators.

1.3 THE SPEED NUMBER shall be written with a prefix 0.

1.4 SPEED NUMBER INTERVALS: Speed numbers shall be expressed arithmetically on a cube-root-of-2 scale. They shall be calculated as described above but shall be rounded off to the nearest cube-root-of-2 step as indicated by the accompanying table.

For a $\log_{10} E$ value between	Speed
(7.05–10) and (7.15–10)	0800
(7.15–10) and (7.25–10)	0640
(7.25–10) and (7.35–10)	0500
(7.35–10) and (7.45–10)	0400
(7.45–10) and (7.55–10)	0320
(7.55–10) and (7.65–10)	0250
(7.65–10) and (7.75–10)	0200
(7.75–10) and (7.85–10)	0160
(7.85–10) and (7.95–10)	0125
(7.95–10) and (8.05–10)	0100
(8.05–10) and (8.15–10)	080
(8.15–10) and (8.25–10)	064
(8.25–10) and (8.35–10)	050
(8.35–10) and (8.45–10)	040
(8.45–10) and (8.55–10)	032
(8.55–10) and (8.65–10)	025
(8.65–10) and (8.75–10)	020
(8.75–10) and (8.85–10)	016
(8.85–10) and (8.95–10)	012
(8.95–10) and (9.05–10)	010

When the log E value is exactly on the border-line of two groups, the group giving the lower speed value shall be used.

2. TESTING TECHNIQUE

2.1 CONDITIONING OF SAMPLE FOR TESTING: The test sample shall be in equilibrium with an atmosphere maintained at a temperature of 20C±5 degrees and a relative humidity of 55±5 percent.

2.2 EXPOSURE:

2.21 TYPE OF SENSITOMETER: The sensitometer shall be a nonintermittent intensity-scale type.

2.22 EXPOSURE TIME:* Exposure time shall be between 1/20 and 1/80 second and shall be accurate to ±1/2 percent.

2.23 MODULATION: The light modulator shall be spectrally nonselective from a wave length of 350 mμ to a wave length of 700 mμ.

The change in exposure with distance along the test strip for either continuous or stepped exposures shall not be greater than a factor of 2 per centimeter.

If stepped increments are used, the exposure increment shall not be greater than a factor of square root of 2 per step.

2.24 LIGHT SOURCE: The quality of this light source shall be that defined by the International Congress of Photography in establishing the international unit of photographic intensity. This includes a tungsten lamp operated at a color temperature of 2360K screened by a specified Davis-Gibson filter. The characteristics of the light source, including composition of the filter, are described in the following publications:

The Unit of Photographic Intensity. The Proceedings of the Seventh International Congress of Photography, July, 1928 (W. Heffer and Sons, Ltd., Cambridge, England).

Filters for the Reproduction of Sunlight and Daylight and the Determination of Color Temperature. RAYMOND DAVIS AND K. S. GIBSON (Bureau of Standards, Miscellaneous Publication No. 114).

2.3 PROCESSING:

2.31 ROLL FILMS AND PACKS

The processing shall be commenced within one hour after exposure. Fresh solutions shall be used.

* The required illumination depends upon the time of exposure chosen. Its value shall be known to an accuracy which will be given in the final specifications.

*2.311 *Developing Solution:*

†Monomethyl para-aminophenol sulfate	2.0 grams
Sodium sulfite (anhydrous)	50.0 "
Hydroquinone	4.0 "
Sodium carbonate (anhydrous)	6.0 "
Potassium bromide	0.75 "
Air-free distilled water to make	1.0 liter

† Sold under such trade names as Metol, Elon, Rhodol, and Pictol.

2.312 *Agitation:* The agitation given the test sample during development shall be the equivalent of that produced by the following method:

The developer is poured into a vacuum flask having an internal length of approximately 22 cm and an internal diameter of about 4 cm. The developer is added until three-quarters of the free space is filled. The negative material to be tested is fastened by means of rubber bands to a glass strip having a width of about 3.5 cm and a length of about 20 cm. The glass strip is fixed to an inert stopper and projects into the flask when the stopper is in place. The stopper carrying the glass strip and test films is inserted in the flask and the development is carried out at the prescribed temperature. During development the vessel is given an oscillatory movement by tilting it in a vertical plane to an angle of about 45 degrees above and below the horizontal. The rate is such that one complete cycle is made in about one second. At the same time the vessel is revolved about its axis, the time for one revolution being about 5 seconds. To terminate development, the films are withdrawn and immediately immersed in the fixing bath.

2.313 *Extent of Development:* The temperature of the developing solution shall be 20C±0.5 degrees. The average gradient, designated by the Greek letter β, for the $\log_{10}$ exposure range from which the speed will be determined (as described under "1. Sensitometric Criterion of Speed") shall be 0.70. In practice this is accomplished by developing for a series of times and interpolating from the family of curves obtained.

* The members of the subcommittee are inclined to believe that this developer, recommended by the British Standards Institution, develops at a rate slightly greater than is desirable for testing purposes. Before the specifications are adopted, a slower acting developer will probably be substituted.

2.314 *Fixing:* The test samples shall be immersed in the following fixing bath immediately after development:

Sodium thiosulfate (Hypo)	400 grams
Sodium bisulfite (or potassium meta bisulfite)	60 "
Water to make	1.0 liter

The fixing solution shall be held at 20C±5 degrees and the fixing time shall be approximately 15 minutes.

2.315 *Washing:* Washing shall be done in water at 20C±5 degrees.

2.316 *Drying:* The samples shall be dried in evenly circulated air maintained at a temperature of 20C±5 degrees.

2.32 MINIATURE CAMERA FILMS*

The processing shall be commenced within one hour after exposure. Fresh solutions shall be used.

2.321 *Developing Solutions:*

†Monomethyl para-aminophenol sulfate	2.0 grams
Sodium sulfite (anhydrous)	80.0 "
Hydroquinone	4.0 "
Borax	4.0 "
Potassium bromide	0.50 "
Air-free distilled water to make	1.0 liter

† Sold under such trade names as Metol, Elon, Rhodol, and Pictol.

2.322 *Agitation:* The same as for Roll Films and Packs.

2.323 *Extent of Development:* The temperature of the developing solution shall be 20C±0.5 degrees. Development shall proceed to such an extent that the average gradient, designated by the Greek letter β, for the $\log_{10}$ exposure range from which the speed will be determined (as described under "1. Sensitometric Criterion of Speed"), shall be 0.60. In practice this is accomplished by developing for a series of times and interpolating from the family of curves obtained.

2.324 *Fixing:* Same as for Roll Films and Packs.

2.325 *Washing:* Same as for Roll Films and Packs.

2.326 *Drying:* Same as for Roll Films and Packs.

* Miniature camera films, of the negative-positive, black-and-white type, are considered to be films not more than 35 mm in width used in still cameras for the making of negatives which normally require enlarged prints.

2.4 DENSITY:

Density shall be computed from the formula:

$$D = \log_{10} \frac{1}{T}$$

where T is the diffuse transmission of the processed sample.

3. USE OF INITIALS ASA

The use of the initials ASA, the words American Standard, or any similar designation, in connection with film speed numbers determined in accordance with these proposed specifications is prohibited during the trial period pending adoption of the method.

APPENDIX

The general problem of determining photographic speed has been divided into three sections:

Section I. Determination of the Speed of a Specific Sample.
- Fundamental Testing Technique.
- Sensitometric Criterion of Speed
- Numerical Evaluation.
- Testing Technique
- Exposure.
- Processing.
- Density Measurement.

Section II. Assigning a Speed Number to a Product as a Whole.
- Number of Samples.
- Age and Storage Conditions of Samples before Testing. Etc.

Section III. Determination of Recommended "Meter Settings" or "Calculator Numbers."
- Adaptation of Film Speeds to Permit Them to Be Used for Calculating Practical Camera Exposures, Taking into Account Such Factors as:
  1. Processing
  2. Film Sensitivity
  3. Measurement or Estimation of Scene Brightness
  4. Etc.

It is recognized that standards must be drawn for all three sections if the whole photographic industry is to derive the maximum benefit from the standardization project. Since each section deals with factors partially independent of the others, standardization can proceed logically by dealing with one section at a time. The proposed specifications in this document deal only with Section I, namely, the Determination of the Speed of a Specific Sample.

CONCEPT OF SPEED

Photographic speed is to be considered as inversely proportional to the minimum camera exposure which a negative material must receive in order that an excellent print may be made therefrom.

In the field of negative-positive, black-and-white materials, this concept implies that speed can be measured by making the best possible print from a series of negatives (which differ only in the exposure given) and then deciding by observation the minimum negative exposure that will lead to an excellent print. Although basically this implication is correct, it is not practical in routine testing, since many prints must be made and a large panel of judges must make a multitude of observations.

A practical method has been found in the field of sensitometry. The method is reasonably simple and rapid to operate, reproducible, and gives results in close agreement with those obtained by the laborious method of making picture negatives and prints.

SENSITOMETRIC CRITERION OF SPEED

The operation of this method is illustrated in Fig. 1. Essentially, it consists of plotting the density-log exposure curve of a material for a given set of conditions (exposure, development, etc.). A log exposure range of 1.50, represented in the figure by the distance AB, is then moved along the horizontal axis from left to right until the slope (or gradient) of the curve at the low end of the range is 0.30 of the average slope over the entire range. When the slope or tangent of angle a is 0.30 of β (*i.e.*, the tangent of angle b) the point C at the low end of the log exposure range represents the exposure value (E) from which the speed of the material is derived.

Speed is then computed by use of the formula

$$\text{Speed} = 1/E.$$

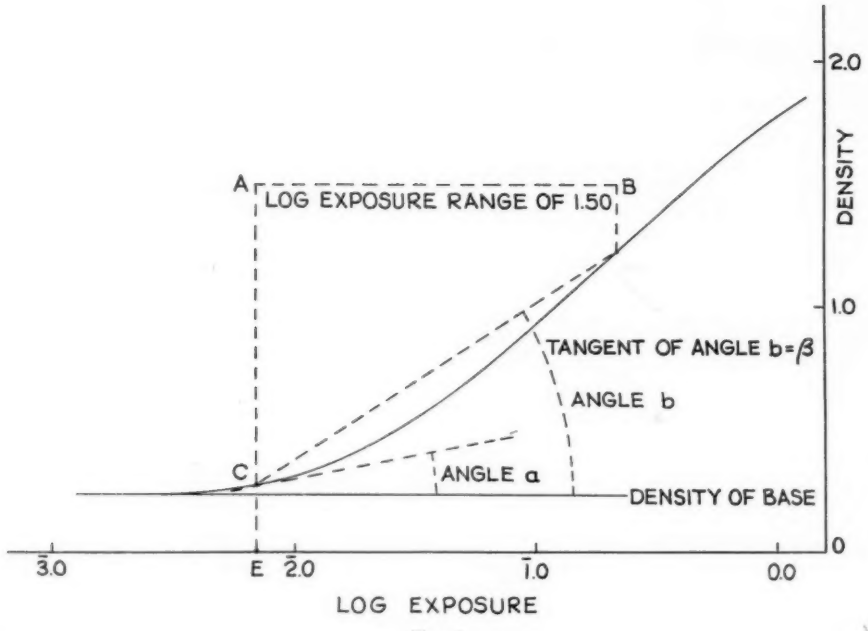


FIG. 1.

The subcommittee proposes the adoption of this sensitometric criterion for determining speed.

Since several systems for determining speed are quite widely used throughout the world, it is felt that speeds measured by using the proposed American sensitometric criterion should be clearly marked to avoid confusion. This may be accomplished by using the prefix 0. For example, if $1/E$ equals 125, the speed would be written 0125.

USE OF SPEED NUMBERS

It should be remembered that speed numbers obtained by the use of the proposed specifications relate to the *minimum* camera exposure which will lead to an excellent print. In normal photographic work it is customary to recommend a somewhat greater exposure in order to allow for uncertainties in exact processing, lighting conditions, camera operation, etc. For that reason these speed numbers are not suitable for direct use with exposure meters or calculators.

The subcommittee intends in the near future to make proposals in connection with Section II (Assigning a Speed Number to a Product as a Whole) and Section III (Determination of Recommended "Meter Settings" or "Calculator Numbers").

The use of the initials ASA, the words American Standard, or any similar designation in connection with film speed numbers determined in accordance with these proposed specifications is prohibited during the trial period pending adoption of the method.